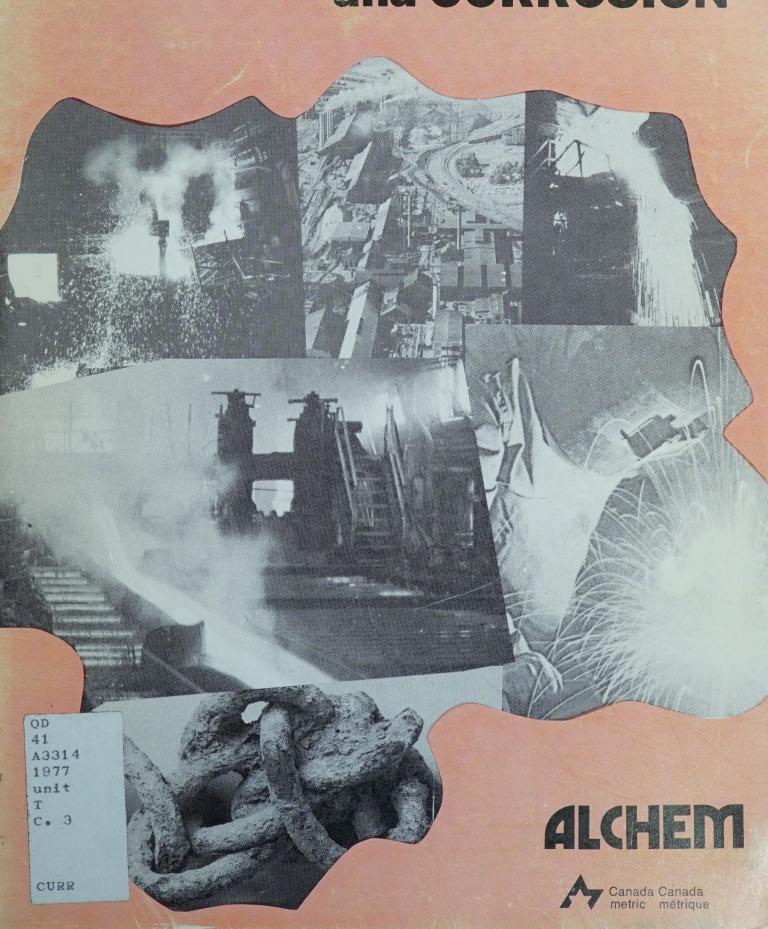


ALLURGY and CORROSION



1. Radioactive Isotopes

Isotope	Half-Life*	Decay Mode**	Isotope	Half-Life*	Decay Mode**
3 H	12.3 a	β-	² 16 Po	0,160 s	α
14 C	5.77 x 10 ³ a	β-	²¹⁸ ₈₄ Po	3.05 min	α,β-
24 Na	15.0 h	β-,γ	²²⁰ ₈₆ Rn	51.5 s	α
32 P	14.3 d	β-	²²² ₈₆ Rn	3.82 d	α
30 S	1.40 s	β ⁺	²²⁴ ₈₈ Ra	3.64 d	α
36 CI	3.00 x 10 ⁵ a	β-	²²⁶ ₈₈ Ra	1.62 x 10 ³ a	α,γ
40 K	1.30 x 10 ⁹ a	β-,γ	²²⁸ ₈₈ Ra	6.70 a	β-
45 20 Ca	1.65 x 10 ² d	β-	²²⁸ ₈₉ Ac	6.13 h	β-
60 27 Co	5.27 a	β-,γ	²²⁸ ₉₀ Th	1.91 a	O;
90 38 Sr	28 a	β-	235 92 U	7.13 x 10 ⁸ a	α,γ
131	8.05 d	β-,γ	²³⁹ ₉₄ Pu	2.44 x 10 ⁴ a	α,γ
212 Pb	10.6 h	β-	²⁴² ₉₅ Am	16.0 h	α,β
² 12 Bi	60.6 min	α ,β-	* s = s min = r h = h	ninutes β	= alpha particle = beta particle += positron
² 12 Po	$3.00 \times 10^{-7} \text{ s}$	α	d = 0	days Y	= gamma photor = alpha & beta

2. Miscel

$$\Delta H_{\text{H}_2\text{O}(s)} \longrightarrow \text{H}_2\text{O}(\ell)$$

$$\Delta H_{\text{H}_2\text{O}(\ell)} \longrightarrow \text{H}_2\text{O}(g) = 40.8 \text{ kJ/mol}$$

$$^{c}H_{2}O_{(s)} = 2.01 \text{ J/(g.°C)}$$

$$^{c}H_{2}O_{(\ell)} = 4.19 \text{ J/(g·°C)}$$

$$^{c}H_{2}O_{(g)} = 2.01 \text{ J/(g·°C)}$$

$$c$$
 = 3.00 x 10⁸ m/s
 e^{-} = $q_{e^{-}}$ = 1.60 x 10⁻¹⁹ C

$$P = Q_e^2 = 1.60 \times 10^{-2} \text{ MoV}$$

$$= 6.02 \times 10^{23} \text{ mol}$$

$$\begin{array}{rcl}
N & = 6.02 \times 10^{23} / \text{mol} \\
Q & = 9.65 \times 10^4 \text{ C/mol}_{\text{e}}
\end{array}$$

$$1C = 6.24 \times 10^{18} \,\mathrm{e}^{-1}$$

*1 V =
$$1 \text{ J/C} = 96.5 \text{ kJ/mole}^{-1}$$

$$*1 t$$
 = 1000 kg = 1 Mg

* exact values

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3. Atomic Molar Masses of Isotopes

⁰ ₁₋ e = 0.000 548 6	$\frac{4}{2} \alpha = 4.00150$	¹⁶ ₈ O = 15.994 91
$^{1}_{1}p = 1.007 \ 276 \ 5$	${}^{4}_{2}\text{He} = 4.002 60$	$^{35}_{17}C1 = 34.96885$
$^{1}_{0}$ n = 1.008 665 0	⁵ ₂ He = 5.012 3	⁵⁶ ₂₆ Fe = 55.934 9
¹ ₁ H = 1.007 825	$\frac{5}{3}$ Li = 5.012 5	$^{206}_{82}$ Pb = 205.974 5
24 - 20140	120 120	210pg - 209 982 9

$$^{3}\text{H} = 3.016\ 05$$
 $^{14}\text{N} = 14.003\ 07$ $^{235}\text{U} = 235.043\ 9$

 $_{2}^{3}$ He = 3.016 03 $^{15}_{7}N = 15.000 11$ $^{238}_{92}U = 238.0508$

		1000	A STATE OF THE PARTY OF THE PAR		
١.	Relative	Strengths of	Oxidizing and	Reducing Agents	**E° (V)

Relative Strengths of Oxidizing and Reducing Agents	**E° (V)
SOA *** $F_{2(aq)}$ + 2e $2F_{(aq)}$	+ 2.87
$MnO_{4(aq)}^{-} + 8H_{(aq)}^{+} + 5e^{-} \longrightarrow 4H_{2}O_{(\ell)} + Mn^{2+}(aq)$	+1.49
$Au^{3+}(aq) + 3e^{-} \longrightarrow Au(s)$	+1.42
***Cl _{2(aq)} + 2e ⁻ 2Cl _(aq)	+1.36
$Cr_2O_7^2(aq) + 14H^+(aq) + 6e^- \longrightarrow 7H_2O_{(\ell)} + 2Cr^{3+}(aq)$	+1.33
$N_2H_{5(aq)}^+ + 3H_{4(aq)}^+ + 2e^- \longrightarrow 2NH_{4(aq)}^+$	+1.27
$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H_{2}O_{(\ell)}$	+1.23
$2IO_{3(aq)}^{-} + 12H_{(aq)}^{+} + 10e^{-} \longrightarrow 6H_{2}O_{(\ell)} + I_{2(aq)}$	+1.19
$Br_{2(aq)} + 2e^{-} \longrightarrow 2Br_{(aq)}$	+ 1.09
$Hg^{2+}(aq) + 2e^{-} \longrightarrow Hg(\ell)$	+0.85
$2NO_{3}^{-}(aq) + 4H_{(aq)}^{+} + 2e^{-} \longrightarrow 2H_{2}O_{(\ell)} + N_{2}O_{4}^{*}(g)$	+0.81
$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(5)}$	+0.80
$Fe^{3}^{+}(aq) + e^{-} \longrightarrow Fe^{2}^{+}(aq)$	+0.77
$O_{2(g)} + 2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2}O_{2(\ell)}$	+0.68
$I_{2(aq)} + 2e^{-} \longrightarrow 2I_{(aq)}$	+0.54
$O_{2(g)} + 2H_{2}O_{(\ell)} + 4e^{-} \longrightarrow 4OH_{(aq)}$	+0.40 the
$Cu^{2+}(aq) + 2e^{-}$ $Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^{-} \longrightarrow Sn^{2+}(aq)$	+0.15 eq
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	+0.40 +0.40
Pb ²⁺ (aq) + 2e ⁻ Pb(s)	-0.13 ength
$Sn^{2+}(aq) + 2e^{-}$ $Sn(s)$	-0.14 gu
Ni ²⁺ (aq) + 2e ⁻ Ni _(s)	-0.23 easi
$Co^{2+}(aq) + 2e^{-} Co(s)$	-0.28
$Cd^{2+}(aq) + 2e^{-} \longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$	-0.41
$\operatorname{Cr}^{3+}(\operatorname{aq}) + 3e^{-} \longrightarrow \operatorname{Cr}(\operatorname{s})$	-0.74
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	-0.76
2H ₂ O _(£) + 2e ⁻ 2OH _(aq) + H _{2(g)}	-0.83
$2NO_{3}(aq) + 2H_{2}O_{(\ell)} + 2e^{-} \longrightarrow 4OH_{(aq)} + N_{2}O_{4(g)}^{*}$	-0.85
$SO_{4(aq)}^{2} + H_{2}O_{(\ell)} + 2e^{-} \longrightarrow SO_{3(aq)}^{2} + 2OH_{(aq)}^{2}$	-0.92
$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^{-} \longrightarrow Mg(s)$	-2.37
Na ⁺ (aq) + e ⁻ Na _(s)	-2.71
$Ca^{2+}(aq) + 2e^{-} \leftarrow Ca(s)$	-2.76
$K^+(aq) + e^- \longrightarrow K(s)$	-2.92
Li ⁺ (aq) + e Li _(S)	-3.04 SRA
(uq) (5)	3101

^{*} Colorless $N_2O_{4(g)}$ decomposes into brown $NO_{2(g)}$.

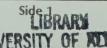
*** Shown as aqueous for convenience; actually measured in gaseous form.

5. Molar Heats of Formation*

		01 1 01111411011
t =	25°C	P = 101 kPa

Name	Formula	Hf (kJ/mol)
acetic acid	CH₃COOH(ℓ)	-488.6
acetone	CH3COCH3(L)	-115.6
acetylene	C ₂ H _{2(g)}	+ 226.9
aluminum oxide	Al ₂ O ₃₍₅₎	-1676.8
ammonia	NH ₃ (g)	- 46.1
benzene	C6H6(2)	+ 82.8
butane	C4H10(L)	-124.8
calcium carbide	CaC _{2(s)}	- 62.8
calcium carbonate	CaCO _{3(s)}	-1205.8
calcium chloride	CaCl _{2(s)}	-795.5
calcium oxide	CaO _(s)	-636.0
carbon dioxide	CO _{2(g)}	-393.6
carbon disulfide	CS _{2(ℓ)}	+ 117.2
carbon monoxide	CO _(g)	-110.5
copper(II) oxide	CuO(s)	-166.6
copper(I) oxide	Cu ₂ O _(s)	-155.3
ethane	C ₂ H _{6(g)}	- 84.6
ethanol	C2H5OH(1)	-277.6
ethene (ethylene)	C ₂ H _{4(g)}	+ 52.3
ethylene dichloride	C2H4Cl2(1)	-166.3
ethylene glycol	C2H4(OH)2(L)	-455.0
ethylene oxide	$C_2H_4O_{(g)}$	- 51.1
glucose	$C_6H_{12}O_{6(5)}$	-900.0
hydrogen chloride	HCl(g)	- 92.6
hydrogen iodide (I _{2(s)})	HI(g)	+ 26.0
hydrogen iodide (I _{2(g)})	HI(g)	- 5.0
hydrogen peroxide	$H_2O_2(\ell)$	-188.0
hydrogen sulfide	$H_2S_{(g)}$	- 20.5
iron(III) oxide	Fe ₂ O _{3(s)}	-822.7
methane	CH _{4(g)}	- 74.9
methanol	CH ₃ OH _(L)	-238.6
nitrogen dioxide	$NO_{2(g)}$	+ 33.9
nitrogen monoxide	NO(g)	+ 90.4
nitromethane	CH ₃ NO _{2(ℓ)}	- 89.2
octane	C ₈ H _{18(L)}	-208.7
propane	C ₃ H _{8(g)}	-103.8
sucrose	C ₁₂ H ₂₂ O _{11(s)}	-1742.0
sulfuric acid	H ₂ SO _{4(.()}	-812.2
sulfur dioxide	SO _{2(g)}	-297.3
2,2,4-trimethylpentane	C8H18(2)	-224.6
sulfur trioxide	SO _{3(g)}	-396.1
vinyl chloride	C ₂ H ₃ Cl _(g)	+ 33.9
water (liquid)	H2O(2)	-286.0
water (vapor)	$H_2O_{(g)}$	-242.0

Refer to the CRC Handbook of Chemistry and Physics for further data.



^{**} Reduction potentials for 1.0 mol/L aqueous solutions at 25°C and 101 kPa.

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Metric Commission Canada has granted use of the National Symbol for Metric Conversion.



TABLE OF CONTENTS METALLURGY AND CORROSION

PART 1 - METALLURGY (T1-T18)

Concentrating the Extracting Metals from Ores T5 Metallurgy in Canada T3 Topics: History of Metallurgy T1 Roasting a Carbonate Ore - Lab T1 T9 Roasting the Ore T7 Separation by Flotation - Demo T1 T6 Refining the Metal T15 Reduction of a Metal - Lab T2 T14 The Hall Process T10 Reducing the Metal T10 Biography: Charles Martin Hall (1863-1914) T16 Allovs T17

PART 2 - CORROSION (T19-T32)

Corrosion of Corrosion of Iron - Lab T3 T21 Equations for Corrosion Reactions T20 Topics: Corrosion T19 Prevention of Corrosion -Sacrificial Anode T30 Cathodic Protection T30 **Protective Coatings T25** Iron T23 Demo T2 T32

PART 3 - OVERVIEW (T33-T36)

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METALLURGY AND CORROSION

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PREFACE Introduction

ALCHEM is the result of many educators joining together to write and teach a chemistry program that would meet the needs of todays students. Through six years of classroom experimentation with over 50 000 students, the program has come to its present form. In answer to the request made by teachers and students throughout the country, ALCHEM has become the most descriptive and applied chemistry material available on the market today.

This approach of applied and descriptive chemistry is integrated into the textual material, labs, demonstrations and classroom exercises to an extent never done before.

Environmental, consumer and industrial chemistry are found throughout the program as well as many historical references and biographies on famous chemists. All this has been achieved without sacrificing a high level of chemistry. The chemistry content is not watered down. You will see from the unique design of the format, that the material has an easy-to-learn-from classroom approach. Students like using the program and their achievement level is high. Test results prove that ALCHEM students have significantly outperformed students on other programs and they have shown an equal or higher interest in chemistry.

Organization of the Program

In its present form there are three core books, ALCHEM 10, ALCHEM 20 and ALCHEM 30, which can be used for two half-courses and one full course, respectively, or with two full courses. Each core book is divided into units that cover specific topics. Within each unit, labs, demos and exercises are integrated in a logical sequence with the textual material. The ALCHEM 20 and 30 each have a complete review unit that acts as a refresher for the student who may not be familiar with previous content. It is our experience that a student can begin the program quite easily even if he or she starts with ALCHEM 30. Each core book can stand on its own.

In addition to the three core books, seven elective units are available to give added dimension to special topics selected by students or teachers. The core units emphasize the concepts of chemistry and bring in the applied and descriptive chemistry where possible. The elective units emphasize the applied and descriptive chemistry and bring in the concepts of chemistry where possible. There is a balance of organic and inorganic electives. The elective units are; Foods and Their Analogs, Athabasca Tar Sands, Analytical Chemistry, Nuclear Chemistry, Metallurgy and Corrosion, Ethylene and its Derivatives, and Alberta Chemical Industries.

The strongest feature in the whole program is that all the material has been reworked and revised many times to make it pedagogically sound for both the student and the teachers. Many new ways of approaching traditionally difficult chemistry concepts have resulted in the student

finding the new approaches easy to understand. For example, the *Gravimetric Stoichiometry* unit is prepared for so thoroughly in the earlier units that it becomes a summary unit. Seven types of bonding in the *Chemical Bonding* unit are explained simply in terms of simultaneous attractions. All questions in the *Energy* unit are done by the approach of heat lost equals heat gained. All redox and acid-base reactions are done by a single five step method.

Another strong feature is the format. In many respects the teacher preparation time has been redirected. The students have the complete program in front of them in their loose leaf binders. Prepared exercises for the student to complete are placed next to the topic covered. Here the organization of the material minimizes the students confusion found in the use of other textbooks. The format of the exercises makes it easier for the teachers to concentrate on classroom strategies. Because quality classroom activities are already developed in the core material and the electives, the teacher has more time to devote to class and individual questions, implementing a wider variety of teaching strategies, spending more professional time on test making and reading, and preparing elective materials.

In addition to the above mentioned texts, an ALCHEM periodic table is available within each core book. Periodic table wall charts are also available. ALCHEM 30 includes the ALCHEM data sheet. Test item banks are available for ALCHEM 10, 20 and 30.

Special Features

The ALCHEM material was developed by the authors in consultation with science curriculum advisors in both education and chemistry at the University of Alberta. Through the years of pilotting, many of the authors and pilot teachers devoted much of their free time and expertise to the improvement and enjoyment of their profession by producing a better chemistry program. ALCHEM serves as a model to what can be accomplished through local curriculum development projects. It also shows what dedicated classroom teachers can do, for without them, we would not have this classroom oriented approach. The over 120 pilot teachers that worked with the program, contributed feedback that is not normally found in other textbook projects. Their comments and criticisms helped make the material work better in the classroom.

For those concerned about the rising cost of textbooks, the ALCHEM prices are very reasonable. In fact, the ALCHEM program costs less than the conventional textbook program even if you amortize the costs of the conventional text over a three to five year period.

The illustrations are of a comic nature to add some fun and enjoyment to the serious chemistry topics. They are designed to bring humor into the classroom—to let the student feel that chemistry does not have to be a heavy subject.

The United States National Institution of Education Curriculum Development Task Force has found that a major reason for the failure of million dollar curriculum projects in the past, has been the lack of significant participation by classroom teachers. ALCHEM is successful because classroom teachers created the program and students find it to be an enjoyable and rewarding learning experience.

The Symons Report has stated that, "A curriculum in this country that does not help Canadians in some way to understand the physical and social environment in which they live and work...cannot be justified in either academic or practical terms. It is essential, from the standpoint of both sound balanced scholarship and of practicality, that studies of the Canadian situation occupy an appropriate place in the curriculum...". ALCHEM is an example of a program that fulfills many of the recommendations made in the Symons Report. ALCHEM is truly a Canadian science program.

The major recommendation of the International Conference on New Directions in Chemistry Curriculum held in 1978 at McMaster University stated that a greater proportion of applied and descriptive chemistry be integrated into chemistry core and elective curriculums and textbooks. In order to accomplish this addition some of the most theoretical topics have to be cut. ALCHEM serves as a unique example of how the applied and descriptive chemistry can be integrated into curriculum materials.

ALCHEM MATERIALS

ALCHEM 10

Unit A: Elements and the Periodic Table
Unit B: Compounds and Nomenclature

Unit C: Chemical Reactions

Unit D: The Mole

Unit E: Gravimetric Stoichiometry

ALCHEM 20

Unit F: Review of ALCHEM 10 Unit G: Chemical Bonding Unit H: Organic Chemistry

Unit I: Solutions

ALCHEM 30

Unit K: Review of ALCHEM 10 & 20

Unit L: Energy

Unit M: Electrochemistry Unit N: Acids and Bases

ALCHEM Electives (Available separately) (level)

Unit J: Analytical Chemistry (20, 30)

Unit O: Foods and Their Analogs (30, 20)

Unit - The Athabasca Tar Sands (30, 20)

Unit P: Ethylene and its Derivatives (30)

Unit S: Alberta Chemical Industries (10)

Unit T: Metallurgy and Corrosion (30)

Unit U: Nuclear Chemistry (30, 20)

Other ALCHEM Materials

- 1. ALCHEM 10 Teachers' Guide
- 2. ALCHEM 20 Teachers' Guide
- 3. ALCHEM 30 Teachers' Guide
- 4. ALCHEM Electives Teachers' Guide
- 5. ALCHEM periodic table (student)
- 6. ALCHEM 30 data sheet (student)
- 7. ALCHEM 10 Test Item Bank
- 8. ALCHEM 20 Test Item Bank
- 9. ALCHEM 30 Test Item Bank
- 10. ALCHEM periodic table (wall chart) Side 1
- 11. ALCHEM periodic table (wall chart) Side 2
- 12. ALCHEM 30 data sheet (wall chart) Side 1
- 13. ALCHEM 30 data sheet (wall chart) Side 2
- 14. Athabasca Tar Sands wall chart
- 15. ALCHEM mole posters
- 16. ALCHEM illustrated, biography wall charts



"MARVIN" The ALCHEM Mole

METALLURGY AND CORROSION UNIT PREREQUISITE KNOWLEDGE AND OBJECTIVES

Prerequisite Knowledge and Skills

Before studying Unit T - Metallurgy and Corrosion - the student should be able to:

- write and balance simple chemical equations, given the chemical names of the reactants and products 1.
- do gravimetric stoichiometry calculations
- define and use the terms oxidation, reduction, oxidizing agent and reducing agent 3.
- write balanced chemical equations for redox reactions, given a table of reduction/oxidation half reactions
- calculate the heat of a reaction, given molar heats of formation data 5.
- calculate the number of moles of electrons when given the current and time
- 7. use a balance and light a bunsen burner
- In general the prerequisite knowledge and skills are fulfilled by the ALCHEM Energy and Electrochemistry Note:

Unit T Objectives

After studying Unit T - Metallurgy and Corrosion the student should be able to:

- define and use the terms metallurgy and smelting
- outline the early history of metallurgy T2
- describe Canada's role as a metal producing nation T3.
- define and use the terms ore, mineral and gangue T4.
- outline the general method for extracting a metal from an ore T5.
- explain the processes concentrating, roasting, reducing and refining T6.
- write balanced chemical equations for roasting and reduction reactions T7.
- given molar heats of formation data calculate the heat of reaction for roasting and reduction reactions T8.
- T9. define and use the term alloy
- T10. describe the production and importance of alloys
- T11. define and use the term corrosion
- T12. given tables of reduction half reactions, write balanced chemical equations for corrosion reactions
- T13. outline the major factors influencing the corrosion of iron
- T14. outline the reaction mechanism involved in the corrosion of iron
- T15. describe the formation of protective coatings on aluminum, zinc, tin, chromium, copper and iron
- T16. describe cathodic protection using impressed currents and sacrificial anodes.

METALLURGY AND CORROSION HISTORY OF METALLURGY

History of Metallurgy

Metallurgy is the science of extracting metals from their naturally occuring compounds and adapting these metals for the use of mankind. The development of metallurgy has been an integral part of the development of civilization. Prehistoric man discovered relatively pure forms of gold and copper as yellow and red nuggets. These nuggets were observed to be different from other pebbles in that they could be pounded into different shapes without cracking or crumbling. The malleability of these metals, i.e., their ability to be pounded into thin sheets without breaking, led to their being shaped into decorative ornaments. Ancient man discovered that a blade made of copper was superior to one made of stone because the copper blade could be pounded to a sharper edge and could be more easily resharpened. The scarcity of native copper (naturally occuring in the metallic state) prevented its widespread use by ancient man.

The shortage of copper was overcome by an accidental discovery. When certain green stones were placed in an ordinary wood fire copper metal was produced. The green stones likely contained the copper compounds we now know as azurite, $Cu(OH)_2 \cdot 2CuCO_3$, and malachite, $Cu(OH)_2 \cdot CuCO_3$. The process of extracting the metallic component of a compound by means of heating is called smelting. The smelting process accidently discovered for copper was improved and used in producing lead, mercury, silver and tin.

One of the problems with using copper metal for tools and weapons is that pure copper does not hold an edge very well. However, when molten copper is mixed with molten tin and the mixture is allowed to solidify, a much harder metal is produced. This mixture of copper and tin is called *bronze*. Such a mixture of metals is called an alloy.

The discovery of bronze occurred about 3800 B.C. somewhere in the Middle East and was likely the result of accidently smelting copper and tin compounds together. The discovery of bronze lead to the production of more durable tools and weapons. The Bronze Age also produced many intricate art objects, some of which have survived to the present day.

Pure iron was only known to the ancients from the few meteorites that fell on the earth from outer space. In about 1500 B.C. the Hittites, living in what is now Turkey, developed a method for smelting iron. The smelting of iron requires higher temperatures than the smelting of copper, lead and tin. Smelting iron involves lining the furnace with charcoal and supplying air with bellows. Pure iron is not very hard but when an iron implement is heated in a charcoal fire, it may pick up enough carbon from the charcoal to form a surface layer of *steel* (an alloy of iron and carbon). The steel surface is harder than the best bronze and holds a sharper edge longer. The development of steel armour, weapons and tools enabled the Hittites to build a large empire.

By 1200 B.C. methods had been developed for refining and alloying the metals; gold, copper, silver, lead, mercury, tin and iron. About 25 centuries elapsed before any new metals were discovered. The date of discovery of a metal is taken as the time that the metal was isolated from one of its compounds so that its properties could be studied. No new metals were discovered until the 13th century when arsenic became known in the metallic state. Although antimony was known from ancient times, it was considered a form of lead and was not recognized as a distinct metal until the 14th century. No other metals were discovered until the 18th century when 13 were isolated. In the 19th century 41 additional metals were discovered. So far in the 20th century 21 new metals have been discovered, 13 of them synthetic. Synthetic elements are produced by bombarding large atomic nuclei (like uranium) with small atomic nuclei (like hydrogen, or oxygen).

The isolation of new metals required an increasingly sophisticated technology. At the same time, the isolation of new metals made possible developments in instruments and techniques by providing metals and alloys with special properties. The modern metallurgist must know what gives a metal its strength, malleability and conductivity and how to get a desired combination of properties in an alloy. The modern metallurgist must also know how to control corrosion in metals and alloys. An understanding of both metallurgy and corrosion is required in order to get the full benefit of the variety of metals and alloys which are now available.

For Questions 1 to 4, use the ALCHEM periodic table of the elements to list the *metals* discovered during the time period indicated.

peri	od indicated.
1.	before the 18th century
2.	the 18th century
3.	the 19th century
4.	the 20th century
5.	What relationship is there between the date of discovery of a metal and the position of the metals on the Relative Strengths of Oxidizing and Reducing Agents Table on the ALCHEM data sheet (inside front cover). Explain.
6.	Define metallurgy.
7.	Define smelting.
8.	Corondinity (the positional II)
0.	Serendipity (the accidental discovery of something valuable) has played a large part in the development of science. List three occasions when serendipity played a part in the development of metallurgy.

METALLURGY AND CORROSION METALLURGY IN CANADA

Metallurgy in Canada

Metallurgy is one of the world's leading industries. Canada is ranked second in the world as a metal producing country. In 1975 Canada produced over 25 different metals and metal oxides with a total value of 4.82 billion dollars. Canada's major metals and their fabricated products were shipped to almost 100 countries in 1975 with export sales totaling 3.88 billion dollars.

Natural Forms of Metals

The forms in which metals are found in nature depend largely on the properties of the individual metals. Metals which are easily oxidized (SRAs) such as magnesium, aluminum, and zinc, are never found free in nature. Metals which are less easily oxidized (WRAs), such as gold, silver and copper sometimes occur in the uncombined state (i.e., are noble metals). Information about the ease of oxidation of metals can be obtained from the Relative Strengths of Oxidizing and Reducing Agents table on the ALCHEM data sheet. The metals are written on the right hand side of the ALCHEM Relative Strengths of Oxidizing and Reducing Agents table with the metals most difficult to oxidize (WRAs) near the top and those easiest to oxidize (SRAs) near the bottom.

Although gold is usually found in the uncombined state, most of the commercial sources of metals are chemical compounds called *minerals*. A mixture of minerals and rocky materials from which at least one of the metals can be extracted at a profit is called an *ore*. The unusable rocky material associated with a valuable mineral is called *gangue* (pronounced "gang"). Once an ore body is located it is mined by either stripping off the overburdened to expose the ore, or by tunneling into the earth to dig out the ore. Table T1 gives some information on the production of metals in Canada.

Exercise:

- 1. Using information from Table T1 on the next page, calculate the world production of aluminum, copper, and iron in 1975.
- 2. In 1975 the industrial price of silver, molybdenum and zinc was respectively, \$132/kg, \$500/kg and \$0.88/kg. Calculate the market value of the 1975 Canadian production of each of these metals.
- 3. Calculate the mass of galena required to give the 1975 Canadian production of lead. Assume 100 % recovery of the metal from the mineral.

Example:

From the molar mass of schalerite, ZnS;
$$1Zn = 1 \times 65.4 = 65.4$$

 $1S = 1 \times 32.1 = \frac{32.1}{97.5} \text{ g/mol}$
Mass $\% = \frac{65.4}{97.5} \times 100 = 67.1\%$
From the percent composition and Table T1; $\frac{67.4}{100} \times 1.09 \times 10^6 \text{ t} = 7.35 \times 10^5 \text{ t Zn}$

4. The Sherritt Gordon Refinery at Fort Saskatchewan, Alberta, produces 45 t/d of nickel metal. What percentage of Canadian production is this?

METALLURGY AND CORROSION METALLURGY IN CANADA Table T1 Production of Metals in Canada

Main Mineral	Formula	Al ₂ O ₃ •xH ₂ O	CuFeS ₂	Au	Fe ₂ O ₃	PbS	CaCO ₃ • MgCO ₁	NIS*2FeS	Ag2S	MoS ₂	ZnS
Main M	Name	bauxite	chalcopyrite	native gold occurs in fine grains or flakes in quartz veins	hematite	galena	dolomite	pentlandite	argentite, (obtained) from ores of lead,	molybdenite	sphalerite
Location of Ore Rodies		not found in Canada in economic concentrations - shipped to Canada from Guiana, Surinam, Malaysia, Attstralia, U.S.A.	Ontario British Columbia Quebec	Ontario Quebec N.W.T.	Newfoundland Quebec Ontario	Yukon British Columbia N. W. T.	Ontario	Ontario Manitoba	Ontario, Yukon, British Columbia, New Brunswick, Quebec	British Columbia Quebec	Ontario, New Brunswick,
1975 Canadian	Production (fonnes)	2.46×10 ⁵	7 26 x 10 ⁵	47.6	9.17.x.10 ⁶	3.51 x 10 ⁵	4.51 × 10 ³	2.45 × 10 ⁵	1.11 x 10 ³	1.27 × 10 ⁴	1.09 x 10 ⁶
Canada's Percentage	of World Production		%6	9%9	2%	% 0	5%	40%	15%	21%	22%
us us	World	33	4	ဗ	ی	Þ	Ą	-	-	2	-
Uses		window frames airplanes packaging	electrical wires plumbing domestic appliances	jewellery dentistry efectronics	construction machines tools	storage batteries anti-knock compounds radiation shielding	lightweight alloys cathodic protection	stainless steel nickel plating coins	photography Jewellery silver plating	high temperature alloys, pigments	die casting galvanizing, brass
Metal		aluminum	copper	pjob	iron	lead	magnesium	nickel	Silver	molybdenum	zinc

METALLURGY AND CORROSION EXTRACTING METALS FROM ORES

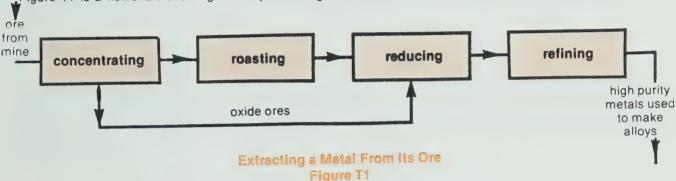
Extracting Metal from Ores

The minimum percentage of metal in the ore which is necessary for a profitable operation varies considerably. Copper ores which contain less than 1 % copper are frequently used while iron ores which contain less than 30 % iron are rarely worked. Many ore contain several different metals. For example, about 90 % of the silver produced in Canada is a by-product of the refining of copper, lead and zinc. The most important minerals are oxides, sulfides, carbonates and halides.

Although the metallurgical processes vary considerably depending on the metal being processed, a general scheme can be presented. The extraction of most metals from their ores consists of four main steps:

- 1. concentrating
- 2. roasting
- 3. reducing
- 4. refining

Figure T1 is a flowchart showing the steps in the general method of extracting a metal from its ore.

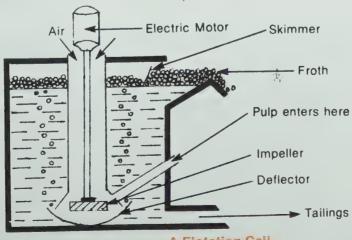


1. Concentrating the Ore

The ores of nonferrous metals generally have a metal content of less than 5%. Extracting the metal directly from such low grade ores is not economical. By applying appropriate procedures, much of the gangue can be removed so that the proportion of metal in the ore is increased to about 30%. The process of treating the ore to remove gangue is called *concentrating* or *milling*. Ore which has been treated in this way is called a *concentrate*.

The first step in making a concentrate is to pulverize the ore. This is followed by one of a number of possible methods of separating the gangue from the ore particles. Separation procedures make use of differences in physical properties between the mineral and the gangue, such as; color, hardness, specific gravity, magnetic properties, electrostatic properties, thermal properties, surface properties and radioactivity. The simplest of these procedures make use of differences in specific gravity. Since rocky materials are generally lighter than the mineral particles they are more easily washed away. Gold panning is an example of this washing process.

The most widely used concentration process is *flotation* which makes use of differences in surface properties between the mineral and the gangue. The flotation process is used to concentrate low grade sulfide ores of copper, lead, nickel and zinc. Mineral particles attach themselves to the bubbles of a froth made by bubbling air up through a cell containing a water suspension of the ore. The efficiency of the process is increased by adding pine oil to increase the amount of froth produced and sodium xanthate to increase the adhesion of the mineral to the froth.



A Flotation Cell Figure T2

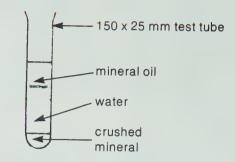
METALLURGY AND CORROSION SEPARATION BY FLOTATION — DEMO T1

Purpose:

To separate a mineral from the gangue

Materials:

- mineral
- sample of crushed lead ore
- 1 150 x 25 mm test tube
- 1 stopper to fit test tube
- 1 test tube rack



Procedure:

- 1. Place a sample of the crushed mineral in a 150 x 25 mm test tube to a depth of about 2 cm.
- 2. Add one-half of a test tube of water and one-quarter of a test tube of mineral oil.
- 3. Stopper the test tube and shake it vigorously for two minutes.
- 4. Allow the test tube to stand in a rack for five minutes.
- 5. Record the observations. Include a diagram of the test tube and its contents.

Observations:

Question:

What differences in physical properties between the mineral and the gangue are involved in this separation process?

METALLURGY AND CORROSION ROASTING THE ORE

2. Roasting the Ore

Following concentration, many ores are *roasted*; i.e., placed in special furnaces where they are heated in a plentiful supply of air. The object of roasting is to drive off any volatile material and in the case of sulfides, carbonates and hydrous oxides to change the mineral to an oxide, which is more convenient to handle in the reduction stage of metallurgy which follows. The equations below show the change that occurs in the roasting of a sulfide, a carbonate and a hydrous oxide, respectively.

roasting sphalerite (a sulfide):
$$2ZnS_{(S)} + 3O_{2}(g) \longrightarrow 2ZnO_{(S)} + 2SO_{2}(g)$$

roasting dolomite (a carbonate):
$$CaCO_3 \cdot MgCO_3(s) \longrightarrow CaO(s) + MgO(s) + 2CO_2(g)$$

roasting bauxite (a hydrous oxide):
$$Al_2O_3 \bullet xH_2O_{(S)}$$
 \longrightarrow $Al_2O_3(s)$ + $xH_2O_{(g)}$

The production of SO_2 gas in the roasting of sulfide ores presents a problem in environmental pollution. In recent years laws have been passed to control the amount of SO_2 emission from this and other industrial processes. The large quantities of SO_2 produced in roasting sulfide ores are used to produce sulfuric acid, a valuable by-product of the metallurgy industry. One of the uses of sulfuric acid is in dissolving copper from low grade copper ores.

Exercise:

Write equations for the following reactions.

- 1. Roasting galena, PbS.
- 2. Roasting argentite, Ag₂S.
- 3. Roasting molybdenite, MoS_2 to form MoO_3 .
- 4. Roasting magnesite, MgCO₃.
- 5. Roasting smithsonite, ZnCO₃.
- Calculate the mass of sulfur dioxide produced by roasting one tonne of galena, PbS. Assume a complete reaction.

Table T2 Heats of Formation of Some Minerals

Mineral	Molar Heat of Formation (kJ/mol)	Mineral	Molar Heat of Formation (kJ/mol)
Ag ₂ S	-31.8	Ag ₂ O	-30.6
MgCO ₃	-1114.5	MgO	-602.7
MoS ₂	-232.5	MoO ₃	-755.6
PbS	-94.4	PbO	-220.0
ZnS	-203.2	ZnO	-348.5

Using heats of formation from Table T2 and from the ALCHEM data sheet, calculate the molar heat of reaction for each ore for the processes described in Question 7 through 9.

- 7. Roasting argentite, Ag₂S.
- 8. Roasting magnesite, MgCO₃.
- 9. Roasting molybdenite, MoS_2 , to form MoO_3 .
- Calculate the mass of zinc oxide that could be produced by roasting one tonne of smithsonite, ZnCO₃.

METALLURGY AND CORROSION **ROASTING A CARBONATE ORE — LAB T1**

Purpose:

To roast a metallic carbonate to a metallic oxide.

Prelab Exercise:

Write a balanced chemical equation for the roasting of basic copper(II) carbonate, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O_{(S)}$ (malachite).

Materials: 1 - crucible tongs 1 - striker 1 - evaporating dish vial of copper(II) carbonate 1 - wire gauze 1 - 10 cm iron ring 1 - scoopula 1 - ring stand 1 - balance 1 - bunsen burner

Note: $CuCO_3 \circ Cu(OH)_2 \circ H_2O_{(S)}$ may have to be substituted for the $CuCO_3$.

Procedure:

- 1. Determine the mass of an evaporating dish and record the mass in the observations section
- 2. Determine the mass of the evaporation dish plus 1.00 g of copper(II) carbonate and record the mass in the observations section.
- 3. Obtain 1.00 g of copper(II) carbonate in the evaporating dish.
- 4. Record the appearance of the copper(II) carbonate in the observations section.
- 5. Place a wire gauze on an iron ring clamped to a ring stand (about 15 cm above the bunsen burner).
- 6. Set the evaporating dish on the wire gauze.
- 7. Light a bunsen burner and adjust the air intake to obtain a small blue cone (about 5 cm high).
- 8. Heat the dish and its contents gently for five minutes, then gradually increase the heat for five minutes (10 cm cone).
- 9. Allow the dish to cool on the gauze, then determine the mass of the dish and its contents and record the mass in the observations section.
- 10. Describe the solid remaining in the dish.

Observations:

mass of empty evaporating dish	1.00 g
mass of copper(II) carbonate	1.00 9
mass of evaporating dish and copper(II) carbonate	
mass of evaporating dish and contents after heating	
appearance of the copper compound before heating	
appearance of the copper compound after heating	

Questions:

- 1. Explain the change in appearance of the copper compound on heating.
- 2. What problems would arise from roasting a sulfide ore in the laboratory?
- 3. Calculate the theoretical yield of copper(II) oxide from the mass of copper(II) carbonate roasted.
- 4. Calculate the percent yield of copper(II) oxide that was obtained.

METALLURGY AND CORROSION REDUCING THE METAL

3. Reducing the Metal

After ores have been concentrated and roasted to convert them to oxides they move into the reduction stage of metallurgy. Ores which were originally oxides move directly from the concentrating stage to the reduction stage as shown in Figure T1. In the *reduction* process the metallic component of a mineral is extracted as a free metal. (In chemical terms, the reduction of a metal involves positive ions changing to neutral atoms by gaining electrons.) *Smelting* is the partial recovery of a metal from a processed ore. Smelting is required to extract the netallic content of an ore and to convert it to a form that is ready for refining.

The reduction of a metal from a mineral requires a reducing agent. Carbon is the most common reducing agent employed in the reduction of metallic oxides. At high temperatures carbon reacts with many metallic oxides to give the free metal and carbon monoxide or carbon dioxide. For example carbon can be used in the reduction of zinc.

$$ZnO_{(s)} + C_{(s)} \longrightarrow Zn_{(s)} + CO_{(g)}$$
2 $ZnO_{(s)} + C_{(s)} \longrightarrow 2 Zn_{(s)} + CO_{2(g)}$

Sometimes carbon is first converted to carbon monoxide by allowing a limited supply of oxygen into the reaction. The carbon monoxide then acts as the reducing agent. For example, carbon monoxide is the main reducing agent in the reduction of iron in a blast furnace.

$$Fe_2O_3(s)$$
 + $3CO_2(g)$ \longrightarrow $2Fe(s)$ + $3CO_2(g)$

Aluminum and hydrogen are used as reducing agents in situations where carbon is unsatisfactory. For example, aluminum is used as the reducing agent in the production of pure manganese because carbon dissolves in metallic manganese. Hydrogen is used in the production of pure molybdenum from its oxide to avoid contaminating the metal with carbon.

The reduction of the more active metals such as sodium, aluminum and magnesium cannot be achieved by chemical means due to the lack of a suitable reducing agent. These metals are generally reduced by the electrolysis of a molten compound of the metal. Usually halides or hydroxides are used in these electrolyses.

The electrolysis of aluminum is of great commercial importance to Canada. Although Canada does not have economic deposits of aluminum ore, the ore is imported from Guyana, Surinam, Malaysia, Australia and the United States. Canada's abundant supply of hydroelectric power is used to electrolyze the metal. In 1975 Canada's five aluminum smelters produced 9.46 x 10⁵ t of aluminum. One of Canada's aluminum smelters is in British Columbia and the other four are in Quebec.

The electrolysis of aluminum is carried out by the Hall Process, named after Charles Martin Hall who divised he process in 1886. In this process an iron box lined with carbon serves as the cathode while carbon rods suspended in the box act as anodes. Since aluminum oxide has a very high melting point (2072 °C) it is not melted in the pure state but is instead dissolved in molten cryolite, Na_3AlF_6 (melting point 1000 °C). When the current basses through this solution the following reactions take place.

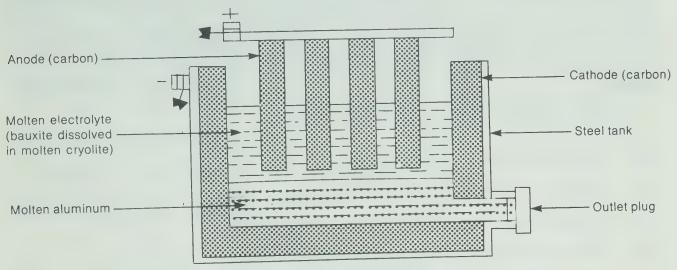
dissociation:
$$2(Al_2O_3(s) \longrightarrow 2Al_3^{2^+}) + 3O_{(cry)}^{2^-})$$

cathode: $4(Al_3^{4^+}(cry) + 3e^- \longrightarrow Al_{(/)})$ (Al m.p., 660 °C)
anode: $3(\frac{2O^2(cry)}{4Al_3^{4^+}(cry) + 6O^2(cry)} \longrightarrow 4Al_{(/)} + 3O_{2(g)})$ (above 1000 °C)
or: $2Al_2O_3(s) \longrightarrow 4Al_{(s)} + 3O_{2(g)}$ (after cooling)

The oxygen produced at the anode reacts with the carbon anode to produce carbon dioxide. The aluminum produced is nearly 100% pure. The heat generated by the current through the cell maintains the temperature of electrolyte above its melting point (1000 °C).

METALLURGY AND CORROSION REDUCING THE METAL

Figure T3 is a diagram of a cell used in the Hall Process for the electrolysis of aluminum oxide dissolved in molten cryolite.



Electrolysis of Aluminum Oxide Figure T3

Exercise on the Hall Process

1. Calculate the maximum mass of aluminum which could be extracted from 1.00 t of aluminum oxide.

2. How long would it take a 500 A current to produce 1.00 t of aluminum metal from an electrolytic cell containing aluminum oxide dissolved in molten cryolite?

3. What mass of oxygen will be produced along with the 1.00 t aluminum metal in Question 2?

METALLURGY AND CORROSION REDUCING THE METAL

General Exercise on Reducing the Metal ore

The exercise below illustrates some of the methods used to reduce the metals listed in Table T1. See a reference book for more details on the processes.

The five step method (see Page T30) introduced in ALCHEM Unit M (Electrochemistry) is applicable for this exercise; however, in most cases there is only one reducing agent and one oxidizing agent. In some cases the reaction involves solids rather than aqueous solutions. The equations for the half reactions for carbon, carbon monoxide and hydrogen as reducing agents are listed below. Assume that these three reducing agent are strong enough to produce a spontaneous reaction when listed in a question. Also assume for Questions 1-10 that the oxidation product of carbon is carbon monoxide. Half-Reactions of Reducing Agents

Example:

Zinc oxide (obtained by roasting zinc sulfide ore) is reduced in a reduction furnace lined with carbon.

Step 1: List species present.
$$SOA \atop Zn_{(s)}^{2^+}, O_{(s)}^{2^-}, C_{(s)}$$

Step 2: Equation for SOA reaction
$$Zn_{(s)}^{2^+} + 2e^- \longrightarrow Zn_{(s)}$$

Step 2: Equation for SOA reaction
$$Zn_{(s)}^{2^+} + 2e^- \longrightarrow Zn_{(s)}$$

Step 3: Equation for SRA reaction. $C_{(s)} + O_{(s)}^{2^-} \longrightarrow CO_{(g)} + 2e^-$

Step 4: Equation for net reaction.
$$Zn_{(s)}^{2^+} + O_{(s)}^{2^-} + C_{(s)} \xrightarrow{spont.} Zn_{(s)} + CO_{(g)}$$

Step 5: (Electrolytic reactions are nonspontaneous; others are assumed to be spontaneous.)

- 1. Aluminum oxide, dissolved in molten cryolite, is electrolyzed in a Hall Cell.
- 6. Molten magnesium oxide is electrolyzed in a commercial electrolytic cell.

 $C_{(s)} + O_{(s)}^{2^{-}} \longrightarrow Co_{(g)} + 2e^{-}$

 $C_{(s)} + 2O_{(s)}^2 \longrightarrow Co_{2(g)} + 4e^{-}$

 $CO_{(g)} + O_{(s)}^2 \longrightarrow CO_{2(g)} + 2e^{-1}$

2. Aqueous copper(II) sulfate is reduced by scrap iron.

7. Molybdenum(VI) oxide reacts with hydrogen gas during the reducing step of extraction.

3. Aqueous gold(III) ions are reduced by aluminum metal.

- 8. Hydrogen gas is used to reduce nickel metal from nickel(II) oxide at a nickel refinery.
- 4. Carbon monoxide reduces iron from iron(III) oxide in a blast furnace.
- 9. Silver chloride reacts with mercury in a silver reduction cell.
- 5. Lead(II) oxide is reduced by the carbon lining in a reduction furnace.
- 10. Zinc oxide reacts with carbon monoxide in a reduction furnace.

METALLURGY AND CORROSION **REDUCING THE METAL**

Using heats of formation from Table T2 and the ALCHEM data sheet, calculate the molar heats of reaction for the metals for the following reduction reactions. Write balanced equations for each half reaction and net reaction. Assume any water produced is in the gas phase and that the oxidation product of carbon is carbon dioxide.

- 11. Hydrogen gas is used to reduce molybdenum metal from molybdenum(VI) oxide.
- 14. Silver is reduced from silver oxide by using carbon as a reducing agent.

- 12. Zinc metal is reduced from zinc oxide using carbon as a reducing agent.
- 15. Carbon monoxide is used to reduce iron from iron(III) oxide.

- 13. Carbon monoxide is used to reduce lead metal from lead(II) oxide.
- 16. Hydrogen gas is used to reduce copper from copper(II) oxide.

Optional:

From the practical reactions used in the above questions approximate where carbon, carbon monoxide and hydrogen (as a group) would appear on a list of relative strengths of reducing agents.

METALLURGY AND CORROSION REDUCTION OF A METAL — LAB T2

P		r	n	^	c	_	
	u	ш	μ	v	J	C	

To reduce a metal from its oxide.

Prelab Exercise:

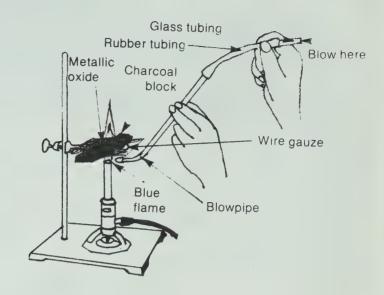
Do Questions 1 and 2 at the bottom of this page.

Prelab Demo:

Demonstrate the use of a blowpipe.

Materials:

- lead(II) oxide powder
- 1 charcoal block
- 1 wire gauze
- 1 10 cm iron ring
- 1 ring stand
- 1 10 cm length of glass tubing
- 1 20 cm length of rubber tubing
- 1 blow pipe
- 1 bunsen burner
- 1 scoopula



Using a Charcoal Block Figure T4

Procedure:

- 1. By rotating the end of a scoopula, make a small cavity in a charcoal block.
- 2. Use the scoopula to obtain enough lead(II) oxide powder to half fill the cavity in the charcoal block.
- 3. Set up a ring stand complete with an iron ring and wire gauze.
- 4. Set the charcoal block on the wire gauze.
- 5. Take a 20 cm length of rubber tubing and insert a 10 cm length of glass tubing in one end. Insert a blowpipe in the other end of the tubing.
- 6. Light a bunsen burner and adjust the air intake to obtain a blue cone.
- 7. Use the blowpipe to direct the flame onto the lead(II) oxide in the charcoal block as shown in Figure T4.

 Caution: Do not inhale through the blowpipe.

 Tilt the gauze and block if necessary.
- 8. Heat the lead(II) oxide until a molten metallic droplet is produced. Record the observations made during the heating process in the observations section.

Observations:

Questions:

- 1. Write the equation for the reduction of lead(II) oxide using carbon as the reducing agent and calculate the molar heat of reaction for the metal produced. (Assume carbon monoxide is one product.)
- 2. What reducing agent besides carbon could be involved in this reaction?
- 3. If 10.0 g of lead(II) oxide were used in this lab, what is the maximum mass of lead that could be produced?

METALLURGY AND CORROSION REFINING THE METAL

4. Refining the Metal

Most metals obtained from primary reduction of their ores in a smelter contain considerable amounts of impurities. The impure metal coming from a smelter is called *matte*. A number of methods are used for the removal of undesirable impurities from the matte. Low melting metals such as tin (m.p. 232 °C) are sometimes refined by melting the impure metal on an inclined table and allowing the molten metal to flow away from the solid impurities. Low boiling metals such as zinc (b.p. 907 °C) and mercury (b.p. 357 °C) are sometimes purified by distillation. At one stage in the refining of iron, air is introduced to burn off sulfur and carbon in the molten iron.

Electrolytic methods of purification are used to obtain high grade nickel, copper, zinc and lead. In *electrolytic purification* a slab of impure metal is used at the anode and pure metal plates out at the cathode. The electrolyte is an aqueous solution of a compound of the metal. The impurities in the anode copper are not brought into solution and fall to the bottom of the cell. The impurities in the metals often include gold and silver which can be extracted later to help pay for the process.

Overview of Extracting Metal from Ores

Define	the	following	terms.

- concentrating the ore
- 2. roasting the ore
- 3. reducing the metal
- 4. refining the metal
- 5. flotation
- 6. smelting
- 7. matte
- 8. electrolytic purification
- 9. mineral
- 10. gangue
- 11. Write equations for the half reactions and the net reaction for the electrolysis of aqueous nickel(II) sulfate.
- 12. Why must metals such as sodium be obtained by electrolysis of a molten salt, whereas metals such as copper may be obtained or purified by electrolysis of an aqueous salt?

METALLURGY AND CORROSION CHARLES MARTIN HALL (1863-1914)



Charles Martin Hall (1863-1914)

Charles Martin Hall was born in Thompson, Ohio, on December 6, 1863. As a teenager Hall was fascinated by chemistry and as a teenager he went to Oberlin College to study the subject. While he was a student at Oberlin college one of Hall's professors remarked that whoever discovered an inexpensive method for extracting aluminum from its ore would become rich and famous and would greatly benefit mankind. Hall's imagination was fired by this remark and he set about finding such a process. After his graduation in 1885, Hall set up a laboratory in the woodshed at his home and began to work on the reduction of aluminum using homemade apparatus (even his batteries were homemade).

Many scientists had tried to reduce aluminum using electricity. Attempts to electrolyze aqueous solutions of aluminum compounds were frustrated by the fact that

water reacts at the cathode in preference to the aluminum ion. The most abundant naturally occuring compound of aluminum is alumina (Al_2O_3) which has a melting point over 2000 °C. This high melting point makes the electrolysis of molten alumina impractical if not impossible. Hall made a breakthrough when he discovered that cryolite (Na_3AlF_6) , which melts at less than 1000 °C, will dissolve alumina. Using a carbon-lined crucible as the cathode and a carbon rod as the anode Hall was able to produce a few globules of molten aluminum in the crucible. Hall made his discovery at the age of 22, just 8 months after graduation from college. Hall received the U.S. patent on his process in 1889. Hall's inexpensive process for reduction of aluminum has caused aluminum to be the most widely used non-ferrous metal in the world today.

At the same time as Hall made his discovery (1886), a Frenchman, Paul Louis Toussaint Heroult (1863-1914), made the same discovery in France. Neither Hall or Heroult knew of the other's work until Heroult applied for a patent for his process in the United States. For this reason the process of electrolytically reducing aluminum from a solvent of molten cryolite is known as the Hall Process in North America and the Heroult Process in Europe.

At first Hall had trouble finding financial backers for his process. Eventually he went to Pittsburg, Pennsylvania, where a small group formed the Pittsburg Reduction Company which has grown into the Aluminum Company of America. Hall spent the rest of his life improving his process and developing the aluminum industry. In 1911 he was awarded the Perkin medal for his work with aluminum. The first aluminum nuggets prepared by Hall are still reverently preserved by the Aluminum Company of America and are called the "Crown Jewels of Oberlin".

Charles Martin Hall died in Daytona Beach, Florida, on December 27, 1914. In his will Hall left three million dollars to his old alma mater, Oberlin College. A life-size statue of Hall, cast in aluminum, stands in one of the laboratories at Oberlin College.

Optional Library Assignment

Canada has no commercial sources of aluminum ore, yet aluminum is refined in Canada.

- 1. Where in Canada is aluminum refined?
- 2. Why were these locations chosen?
- 3. What is the source of raw materials and electricity at each location?

METALLURGY AND CORROSION ALLOYS

Alloys

The metals used by mankind are almost exclusively alloys rather than pure metals. Copper used for electrical purposes is an exception to the rule. An *alloy* may be defined as a combination of two or more elements which has metallic properties. Alloys are commonly prepared by smelting together the component metals and allowing the molten mass to solidify.

An alloy may be a solid solution, a heterogeneous mixture or an intermetallic compound. When a solid solution forms, the metallic crystals contain atoms of both elements. Gold and silver form solid solutions with each other in all proportions. In some cases, crystals of the pure metals may separate so that the alloy is a heterogeneous mixture containing tiny crystals of the constituent elements. Alloys of lead and antimony are usually heterogeneous mixtures. In other cases, the metals may react to form an intermetallic compound. It is not possible to predict the formulas of these intermetallic compounds from simple bonding theory. Some examples of intermetallic compounds, whose formulas have been determined experimentally, are $\operatorname{Cu_3Al}$, $\operatorname{Fe_5Zn_{21}}$, $\operatorname{Cu_5Zn_8}$, $\operatorname{Cu_5Sn}$ and $\operatorname{Cu_2Mg}$. Alloys are very often combinations of solid solutions, heterogeneous mixtures and intermetallic compounds.

By variation in composition and method of preparation, a series of alloys with a wide range of properties may be obtained. The relationship between the properties of a given alloy and its composition is very complex, but a few general comments may be made. Many alloys have lower melting points than any of their components. The electrical conductivity of an alloy is poorer than that of the pure metals. For example, brass (a Cu-Zn alloy) is a much poorer conductor than copper and nichrome (a Ni-Cr alloy) wire is noted for its high electrical resistance. Alloys are generally harder and more resistant to corrosion than the pure metals. The difference in properties between alloys and pure metals is most pronounced in the alloys that contain intermetallic compounds. Table T3 lists some important alloys.

Exercise:

1. What is the percentage composition by mass for the intermetallic compounds, Cu₅Zn₈ and Cu₂Mg?

Example:
$$Cu_3AI$$
 $3Cu = 3 \times 63.5 = 191$
 $1AI = 1 \times 27.0 = 27.0$
 $molar mass = 218 g/mol$
 $Cu = 191 \times 100 = 87.6\%$
 $Cu = 191 \times 100 = 12.4\%$
 $Cu = 191 \times 100 = 12.4\%$

2. An intermetallic compound of copper and tin contains 27.3% tin by mass. What is the chemical formula of this metallic compound? (Assume 100 g of compound and calculate the number of moles of each metal.)

- 5. Which alloys are noted for being hard?

METALLURGY AND CORROSION ALLOYS

Table T3
Some Important Alloys

Alloy	Approximate (%) Composition (mass)	Properties	Uses
Sterling Silver	92 % Ag, 8 % Cu	corrosion resistant	silverware, jewelry
Wood's Metal	50 % Bi, 25 % Pb, 12 % Cd, 12 % Sn	low melting point (68 °C)	fire extinguishers (sprinklers)
Bronze	92 % Cu, 6 % Sn, 2 % Zn	high resistance to wear	statuary, plumbing fixtures
Brass	70 % Cu, 30 % Zn	corrosion resistant, easily worked	plumbing fixtures, keys
German Silver	50 % Cu, 30 % Ni, 20 % Zn	corrosion resistant	imitation silver
Wrought Iron	99.5% Fe, 0.5% C	soft, can be cast, welded or forged	railings, nails, sheets
Cast Iron	97 % Fe, 3 % C	very hard, can be cast	bases, castings, columns
Chrome Steel	97 % Fe, 3 % Cr	hard, tough, elastic, corrosion resistant	ballbearings, files
Vanadium Steel	97 % Fe, 3 % V	high elasticity high tensile strength shock resistant	auto parts, tools, wrenches
Molybdenum Steel	95% Fe, 5% Mo	very hard, high tensile strength, corrosion resistant	axels, lathe tools
Nickel Steel	94% Fe, 6% Ni	hard, tough, elastic, corrosion resistant	armorplate, steam engine parts
Stainless Steels	60-82 % Fe, 10-20 % Cr, 8-30 % Ni	corrosion resistant (some stainless steels are not magnetic)	surgical instruments, kitchen ware
Manganese Steel	88% Fe, 12% Mn	hard, tough	safes, rock-crusher jaws
Alnico	63% Fe, 20% Ni, 12% Al, 5% Co	high magnetic	permanent magnets
Monel Metal	60% Ni, 33% Cu, 6.5% Fe, 0.5% Al	corrosion resistant, high tensile strength	turbine blades, pump bodies
Babbit Metal	90 % Sn, 7 % Sb, 3 % Cu	low coefficient of friction	bearings
Solder	60% Sn, 40% Pb	low melting point (183 °C)	joining metals

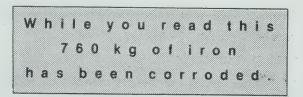
METALLURGY AND CORROSION CORROSION

Corrosion

Corrosion refers to the conversion of metals or alloys to their compounds, usually oxides, carbonates or sulfides. In a sense corrosion represents a return of the metal to an ore-like state, with complete loss of its metallic properties. Most naturally occurring ores are oxides, carbonates or sulfides. Energy is required to convert these ores to metals. Corrosion, the reverse process, requires no such supply of energy so that the formation of the corrosion compound occurs spontaneously under certain conditions. Metals vary greatly in their susceptibility to atmospheric and chemical corrosion. Those metals that are most easily obtained from their ores and require the least energy in smelting are generally less prone to corrosion. Those metals that are reduced with most difficulty tend to revert most readily to their natural state.

Corrosion is of considerable economic consequence with an estimated 20% of the iron and steel produced annually going to replace that lost by corrosion. Corrosion studies are undertaken to reduce the economic losses due to the corrosion of pipes, tanks, cars, machines, bridges, etc. Studies are required to improve the safety of operating equipment such as pressure vessels, boilers, turbine blades and airplane components which can fail through the results of corrosion. Corrosion studies are also important from the point of view of conservation of the world's limited metal resources and the energy and water reserves required to produce the metals.

At an exhibition dealing with corrosion in 1937, the following poster was displayed.



Exercise:

Use Table T1 to calculate the 1975 value for Canada and the world for the above poster. Assume 20 % off all iron and steel produced annually is lost to corrosion and assume the poster takes 5 s to read.

Oxidizing Agents

The corrosion process involves the oxidation of metals. In oxidation, metal atoms lose electrons to form the positive ion in an ionic compound. The most common oxidizing agent for corrosion reactions is oxygen gas from the atmosphere. The oxygen may react by itself or it may react in conjunction with water.

Active metals such as aluminum and magnesium react readily with oxygen in the atmosphere, as shown by the following reactions.

$$4AI_{(S)} + 3O_{2(g)}$$
 $2AI_{2}O_{3(S)}$
 $2Mg_{(S)} + O_{2(g)}$ $2MgO_{(S)}$

The oxide film which forms on the surface of the aluminum adheres tightly to the surface of the metal and prevents further corrosion. The oxide film that forms on magnesium metal is not quite so impervious but it does slow further oxidation.

METALLURGY AND CORROSION **EQUATIONS FOR CORROSION REACTIONS**

Very often, corrosion takes place in aqueous solution. Although the solutions involved are rarely at standard conditions, the Relative Strengths of Oxidizing and Reducing Agents table on the ALCHEM data sheet is a useful guide in determining possible corrosion reactions. Two additional reduction half reactions which are valuable in corrosion studies involve the gases, carbon dioxide and hydrogen sulfide.

$$CO_{2}(g) + H_{2}O_{(I)} + 2e^{-}$$
 $H_{2}(g) + CO_{3}^{2}(aq)$
or (s)
 $H_{2}S_{(g)} + 2e^{-}$
 $H_{2}(g) + S_{3}^{2}(aq)$
or (s)

Oxidation-reduction half reaction can be used to write equations for many corrosion reactions.

Example:

Silver tarnishes in the presence of hydrogen sulfide gas. The reaction takes place in dry air.

reduction:
$$\begin{array}{c} SOA \\ Ag(s) \\ SRA \\ H_2S(g) \\ + 2e^- \\ \end{array}$$

$$\begin{array}{c} H_2(g) \\ + S^2(s) \\ \end{array}$$
 oxidation:
$$\begin{array}{c} 2(Ag(s) \\ \hline \end{array}$$

$$\begin{array}{c} Ag^+_{(S)} \\ + e^- \end{array}$$

$$\begin{array}{c} H_2(g) \\ + 2Ag^+_{(S)} \\ \end{array}$$

$$\begin{array}{c} H_2(g) \\ + 2Ag^+_{(S)} \\ \end{array}$$

$$\begin{array}{c} H_2(g) \\ \end{array}$$

Write equations for the following corrosion reactions. (Write half-reaction equations followed by a net equation).

- 1. A lead pipe reacts with an acidic solution.
- Bromine vapor in a fume hood corrodes the nickel plating on a ring stand. 2
- Magnesium metal reacts with water. 3.
- Zinc metal is corroded by the action of air and water.
- Copper tarnishes in the presence of hydrogen sulfide.

Purpose:

To investigate some of the factors influencing the corrosion of iron.

Materials:

- steel wool
- 50 mL of acetone
- 1 100 mL beaker
- 12 10 cm lengths of iron wire
- 10 13 x 100 mm test tubes
- 2 18 x 100 mm test tubes
- 2 rubber stoppers
 - (to fit 18 x 150 mm test tubes)
- 1 test tube rack

- 1 10 cm length of magnesium ribbon
- 1 10 cm length of copper wire
- 1 2 cm length of transparent tape
 - 30 mL of distilled water
- 25 mL of deaerated water (freshly boiled)
- 6 mL of 0.01 mol/L CuSO, (aq)
- 6 mL of 0.01 mol/L HCl(aq)
- 6 mL of 0.01 mol/L NaCl(aq)
- 6 mL of 0.01 mol/L NaOH(aq)
- 6 mL of 0.01 mol/L K₂Cr₂O₇ (aq)

Procedure:

Day 1:

- 1. Obtain about 50 mL of acetone in a 100 mL beaker.
- Obtain twelve, 10 cm lengths of iron wire and a piece of steel wool. Clean each length of iron wire with the steel wool and wash them with acetone. Set the wires on a paper towel to dry.
- Obtain ten 13 x 100 mm test tubes and two 18 x 150 mm test tubes in a test tube rack.
- Use five of the 13 x 100 mm test tubes to obtain about 6 mL of each of the following solutions: $0.01~\text{mol/L CuSO}_{4\,(aq)},\,0.01~\text{mol/L HCl}_{(aq)},\,0.01~\text{mol/L NaCl}_{(aq)},\,0.01~\text{mol/L NaOH}_{(aq)}~\text{and}~0.01~\text{mol/L NaOH}_{(aq)}$ K₂Cr₂O_{7 (aq)} (6 mL is a 13 x 100 mm test tube one half full).
- Place a clean, dry iron wire into each of the solutions in Step 4.
- Obtain about 30 mL of distilled water in a 100 mL beaker. Pour about 6 mL of the distilled water into 5 different 13 x 100 mm test tubes. Place a clean, dry iron wire into one of these test tubes.
- Take four pieces of clean, dry iron wire. Coil a 10 cm length of magnesium ribbon around one piece of iron wire. Coil a 10 cm length of copper wire around a second piece of iron wire. Wrap a 2 cm length of transparent tape around the middle of a third iron wire. Bend the fourth piece of iron wire in half. Place each of the four pieces of iron wire into a different one of the four test tubes of distilled water prepared in Step 6.
- Fill a 18 x 150 mm test tube with deaerated water. Place a clean, dry iron wire into the test tube and stopper 8.
- Place a clean, dry iron wire into a dry 18 x 150 mm test tube and stopper it.
- 10. Record any observations in the observation table.
- Allow the test tubes to stand overnight in the test tube rack.

Day 2:

- 12. Examine each of the test tubes and record all observations in the observation table.
- 13. Remove the magnesium, copper and tape wrappings. Discard the tape, but straighten and return the magnesium and copper.

METALLURGY AND CORROSION CORROSION OF IRON — LAB T3

Observations:

1.

6.

7.

10.

11.

12.

	Obse	rvations
Test Tube	Day 1	Day 2 or Later
0 01 mol/L CuSO _{4 (aq)}		
0.01 mol/L HCl _(aq)		
0.01 mol/L NaCl _(aq)		
0.01 mol/L NaOH _(aq)		
0.01 mol/L K ₂ Cr ₂ O _{7 (aq)}		
distilled water		
wire wrapped with Mg		
wire wrapped with Cu		
wire wrapped with transparent tape		
bent wire		
deaerated water		
dry air		

Questions:

1.	Which iron wire corroded most?	
2.	Which iron wire corroded least?	
3.	Which test tube is the control? _	

4. What generalizations can be made about the corrosion of iron?

5. Write a couple word explanation for each observation?

METALLURGY AND CORROSION CORROSION OF IRON

Rusting of Iron

The corrosion of iron deserves particular attention because of the importance of iron and steel as structural materials. A careful study of the corrosion of iron indicates that both oxygen and water must be present for rapid rusting at ordinary temperatures. It is also observed that the corrosion of iron is accelerated by the presence of electrolytes (especially acids), contact with less active metals, strains in the metal and the presence of rust itself.

A complex reaction, like the rusting of iron, takes place in a series of steps called a *reaction mechanism*. The sum of the steps in the reaction mechanism gives the overall reaction. The following reaction mechanism has been proposed for the rusting of iron.

Step 1:
$$4(Fe_{(s)})$$
 $Fe_{(aq)}^{2+} + 2e^{-}$
Step 2: $8(H_{(aq)}^{+} + e^{-})$ $H_{(aq)}$
Step 3: $2(4H_{(aq)} + O_{2(g)})$ $2H_{2}O_{(I)}$
Step 4: $4Fe_{(aq)}^{2+} + O_{2(g)} + 10H_{2}O_{(I)}$ $2Fe_{2}O_{3} \cdot 3H_{2}O_{(s)} + 8H_{(aq)}^{+}$
Overall: $4Fe_{(s)} + 3O_{2(g)} + 6H_{2}O_{(I)}$ $2Fe_{2}O_{3} \cdot 3H_{2}O_{(s)}$

In Step 1 the iron loses two electrons to form iron(II) ions. Step 1 cannot proceed far without some means of removing electrons. Most aqueous solutions contain at least a small concentration of hydrogen ions that can pick up these electrons as shown in Step 2. The hydrogen atoms formed in Step 2 might be expected to form hydrogen molecules, but hydrogen gas is not observed in rust formation in neutral solutions. Since iron is a good catalyst for hydrogenation reactions, it is likely that hydrogen atoms react with oxygen molecules and water to form rust and to regenerate the hydrogen ions. Note that hydrogen ions are a catalyst for this reaction since they accelerate Step 2 and are regenerated in Step 4.

The mechanism proposed for the corrosion of iron accounts for the observations made about rusting. The observation that both oxygen and water are necessary for the formation of rust is accounted for by Steps 3 and 4. This explains why the rusting of exposed iron is almost negligible when the relative humidity is less than 50 %. For example, in Delhi, India, there is an iron pillar which is about fifteen hundred years old. Although the metal is unprotected it has scarcely deteriorated because of the dry unpolluted atmosphere. In general, atmospheric corrosion of iron becomes significant when the relative humidity is above 60 %. The proposed mechanism for iron corrosion also explains why the corrosion of cast iron boilers is slow when the hot water is deaerated.

Rusting is more rapid in the presence of electrolytes which can function as charge carriers and accelerate Steps 1 and 2. For this reason ships rust more rapidly in seawater than in fresh water and cars rust more rapidly where sodium chloride is present from winter salting of roads. In addition the chloride ions inhibit the formation of a protective oxide coating. If a hydroscopic compound like calcium chloride is used in salting roads, the moisture retained in the hydrated calcium chloride expedites Step 4.

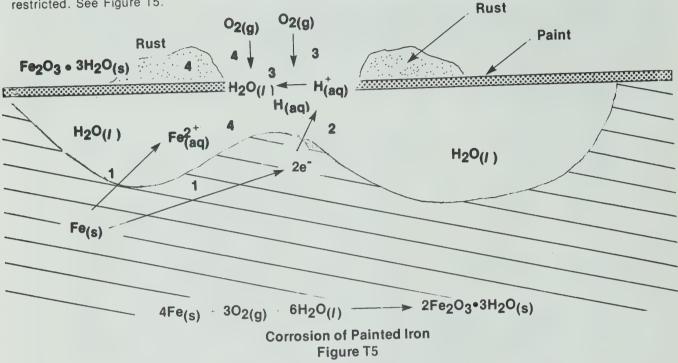
Corrosion of iron is particularly rapid in acidic solutions and hydrogen gas is generally evolved. This observation is accounted for by Step 2. The higher concentration of hydrogen ions results in sufficient hydrogen atoms to form hydrogen gas. Air pollutants such as sulfur dioxide and nitrogen oxides form acids in water and increase the corrosive action of rainwater. Rainwater having a pH as low as 4 has been reported. Such acid rains can cause the metal on cars to corrode rapidly.

When iron and copper pipes are connected the iron rusts more rapidly than usual. A household example of this is the connection between a copper water pipe and a steel water tank. Electrons released by the formation of iron(II) ions in Step 1 repel each other and flow from the iron to the copper. This removes the excess negative charge from the iron and allows more iron(II) ions to form. Aqueous hydrogen ions are attracted to the copper and are reduced. Hydrogen atoms do not adhere as well to copper as they do to iron and as a result, Step 3 of the proposed mechanism is accelerated.

The observation that rusting is most severe around points of stress or strain in the metal is probably due to the continual breaking of the protective oxide coat, exposing the underlying metal to more oxidation. The acceleration of rusting by the presence of rust itself is likely the result of the water retained in the rough corroded

METALLURGY AND CORROSION CORROSION OF IRON

One of the strongest supports for the stepwise rusting mechanism comes from observations on painted steel. When the paint coat is scratched or broken, the steel corrodes underneath the paint where the oxygen supply is restricted. See Figure T5.



Where the oxygen supply is limited, iron(II) ions diffuse before encountering enough oxygen to be oxidized to iron(III) ions, forming the hydrated iron(III) oxide as shown in Step 4 (Fe²⁺(aq) + $O_2(g)$ + $10H_2O_1(g)$ = $2Fe_2O_3 \cdot 3H_2O_1(g)$). This means that the rust may deposit some distance away from the point where *pitting* (eating away the metal surface) occurs, thus preventing the formation of a protective oxide coating on the metal. The result is that the rust forms on the surface of the paint where the oxygen is plentiful and pitting occurs under the paint where the oxygen supply is restricted. A small spot of rust on a fender is usually a sign of a more serious problem under the paint.

Exercise:

1. Write the reaction mechanism and the overall reaction for the corrosion of iron.

- 2. Why is the corrosion of car bodies worse in cities that use salt on the streets in the winter than in cities that do not use salt?
- 3. Why are copper straps (rather than iron straps or bent over nails) used to hold household copper water lines in place?
- 4. When an iron post is immersed in water rust forms at the water line and the iron post pits below the water line. Explain why this happens.

METALLURGY AND CORROSION PROTECTIVE COATING

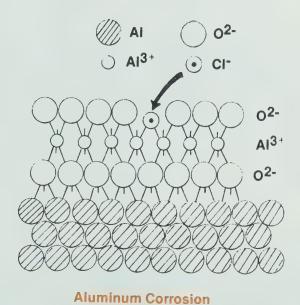
Protective Coating

In order to minimize the damaging effects of corrosion, a number of techniques have been developed to protect the metal. The most direct means is to coat the surface of the metal to prevent its contact with oxidizing agents. One way of doing this is to coat the surface of the metal with grease, paint, or plastic. As already noted, some metals form an outer passive coat when exposed to the environment. With other metals, the protective coating can be formed by treatment with certain chemicals.

1. Aluminum

Aluminum airplanes, cooking pots, and pop cans last a long time despite the ease of oxication of aluminum. When aluminum is exposed to air a tightly adhering layer of aluminum oxide rapidly forms. The crystal structure of aluminum oxide and aluminum metal is such that there is essentially a perfect fit between the oxide layer and the metal. Because of this oxide layer, aluminum becomes more difficult to oxidize than copper and almost as difficult as silver. If the metal surface is scratched, the oxide layer rapidly reforms.

However, aluminum undergoes significant corrosion in the presence of the chloride ion. The crystalline continuity between aluminum and its oxide is disrupted by the presence of an occasional chloride ion. Wherever such disruptions occur the oxide coating is broken and the break develops into an area where further oxidation of aluminum occurs.



2. Zinc

Zinc also might be expected to undergo easy oxidation but when exposed to the atmosphere it reacts with carbon dioxide and water to form a passive coating of basic zinc carbonate, $ZnCO_3 \bullet Zn(OH)_2$. The formation of basic zinc carbonate can be represented by the following equations.

Figure T6

oxidation:
$$Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$$

reduction: $CO_{2}(g) + H_{2}O_{(I)} + 2e^{-} \longrightarrow H_{2}(g) + CO_{3}^{2-}(aq)$
overall: $Zn_{(s)} + CO_{2}(g) + H_{2}O_{(I)} \longrightarrow H_{2}(g) + Zn_{(aq)}^{2+} + CO_{3}^{2-}(aq)$
 $Zn_{(s)} + CO_{3}(s)$

METALLURGY AND CORROSION PROTECTIVE COATINGS

oxidation:
$$Zn_{(S)} \longrightarrow Zn^{2}_{(aq)}^{+} + 2e^{-}$$

reduction: $2H_{2}O_{(I)} + 2e^{-} \longrightarrow 2OH_{(aq)}^{-} + H_{2}(g)$
overall: $Zn_{(S)} + 2H_{2}O_{(I)} \longrightarrow Zn^{2}_{(aq)}^{+} + 2OH_{(aq)}^{-} + H_{2}(g)$

The zinc carbonate and zinc hydroxide are formed simultaneously and they combine to form a basic carbonate.

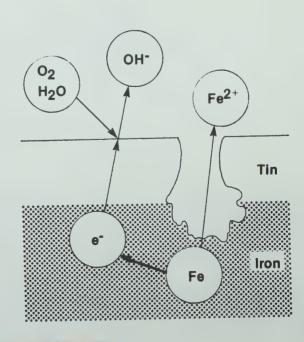
$$ZnCO_3(s) + Zn(OH)_2(s) \longrightarrow ZnCO_3 \cdot Zn(OH)_2(s)$$

Zinc can be used to protect steel from corrosion. In a process called *galvanizing*, steel has a thin coating of zinc applied to all sides of it. The zinc can be applied by dipping, spraying or electrodeposition. On contact with air the zinc forms a protective coating of basic zinc carbonate. Since zinc is more easily oxidized than iron, if the zinc surface is broken so that both zinc and iron are exposed, it is the zinc that is preferentially oxidized. The protective coating that forms on the exposed zinc covers the steel as well. Cadmium can be used in a similar manner as a *sacrificial* coating.

3. Tin

Tin forms a self protecting oxide coat on exposure to air which accounts for its use in making tin cans. Manufacture of tin cans consists of coating steel cans with a layer of tin. Tin is generally electrodeposited because this produces a thin, uniform layer relatively free from defects. Even if tin does react with the contents of the can, the non-toxic nature of tin compounds makes tin plate ideal for handling beverages and foods. However, if the tin coating is broken the underlying steel oxidizes more readily than the tin and rusting proceeds more rapidly than if the steel had been unprotected. The situation here is analogous to the corrosion of iron pipes which are connected to copper. The electrons released by the oxidation of the iron flow to the tin and accelerate the oxidation of the iron.

Tin forms a noble coating and iron corrodes first wherever a crack in the tin layer forms.

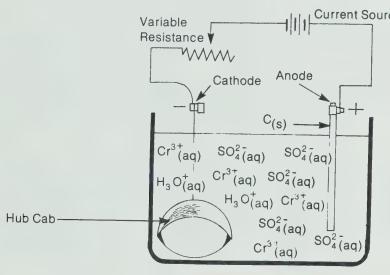


Corrosion of a Tin Can Figure T7

METALLURGY AND CORROSION PROTECTIVE COATINGS

4. Chromium

On exposure to air chromium forms a protective oxide coating that has the additional advantage of taking a high polish. The "chrome" decorations on cars are made of steel which has been electroplated with chromium, usually with intervening layers of copper and nickel to improve adhesion and durability. Unprotected chromium is more easily oxidized than iron, but with its passive oxide layer chromium is less easily oxidized than iron. When the chrome plating on a car is scratched, exposing the chromium and the iron, the chromium forms a passive oxide coating. This oxide coating is very thin and does not cover the exposed iron. The exposed iron corrodes in preference to the passivated chromium.



The SO_4^2 (aq) ion or the SiF_6^2 (aq) ion catalyzes the chromium electroplating. The relative concentration of the CrO_4^2 (aq) ion and the catalyzing ion is very important. Chromium plating requires a very exacting process.

Chromium Plating Figure T8

Copper

Copper exposed to the atmosphere would not be expected to corrode to any great extent because it is quite difficult to oxidize. (Recall the ease of reduction of copper.) The corrosion of copper is further inhibited by the formation of a basic copper(II) carbonate, $CuCO_3 \cdot Cu(OH)_2(s)$, layer. This layer, called *patina*, creates the green color of weathered copper roofs and bronze statues.

6. Iron

Unlike the passive oxide, carbonate and hydroxide coatings already mentioned, that of iron does not normally adhere well to the metal surface. The reddish oxide found on untreated iron slowly flakes off, exposing additional metal for corrosion. In addition the oxide layer retains moisture which accelerates rusting. However, iron can be passivated by suitable chemical treatment. For example, concentrated nitric acid oxidizes the surface of iron to a layer of iron(III) oxide which protects the surface from further corrosion. If the oxide coating is scratched there is a rapid attack on the underlying metal.

A more permanent "gun blue" protective layer can be obtained by dipping the iron into a strong oxidizing agent such as molten potassium nitrate. These thicker passive coatings are composed of adherent, hard layers of Fe₃O₄ (Fe₂O₃•FeO). Another way of producing protective oxide coatings on iron is by using dilute solutions of oxidizing agents such as potassium dichromate or sodium chromate. Chromate compounds are frequently used as rust inhibitors in circulating water coolers. Anticorrosion paints contain oxidizing agents such as zinc chromate, lead(II) chromate, or mercury(II) oxide which react with the iron to form a protective oxide layer.

Most iron alloys are more resistant to corrosion than is pure iron. In alloys containing as little as 1 % carbon, phosphorus, sulfur, nickel, chromium, or copper, the rust films tend to be compact and adherent. The best known corrosion resistant iron alloys are the stainless steels which contain at least 10 % chromium. The oxidation of chromium to form a film of chromium(III) oxide provides a high corrosion resistance to these alloys. Most stainless steels contain nickel as well as chromium with compositions as high as 20 % of each metal. Although stainless steels are resistant to rusting under most conditions, they will corrode in environments containing appreciable concentrations of chloride or bromide ions. (Note the similarity to aluminum in this regard.)

METALLURGY AND CORROSION **PROTECTIVE COATINGS**

Exercise

- 1. Why do aluminum pots and pans develop a pitted surface when table salt is added to the cooking water?
- Write the equations for the half reactions and net reaction for the formation of patina on the surface of copper which is exposed to the atmosphere.

3. Commercial gun bluings contain the following chemicals. Identify all the oxidizing agents in the mixture and explain how the mixture protects a gun barrel from rusting.

H ₂ O	82.3%	HgCl ₂	2.4%
C ₂ H ₅ NO ₂	6.5%	FeCl ₃	0.9%
KNO ₃	3.5%	NaNO ₃	0.9%
KCIO ₃	3.0%	CuCl ₂	0.5%

4. When cans are taken to the garbage dump, the tin cans decompose more quickly than the aluminum cans. Explain why this happens.

METALLURGY AND CORROSION CATHODIC PROTECTION

Cathodic Protection

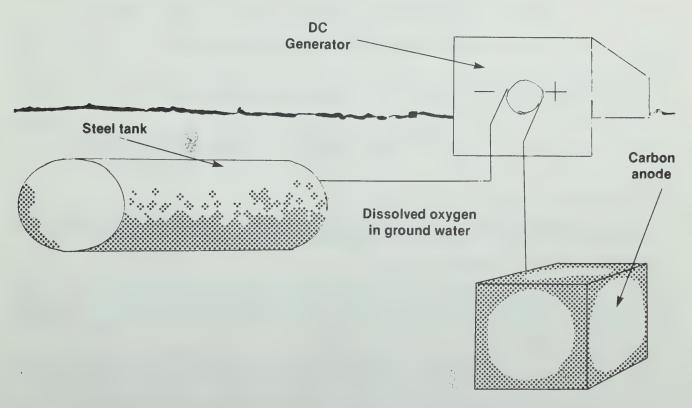
During corrosion the metal is oxidized, that is, it undergoes the same chemical change as the anode of an electrochemical cell. One effective way of preventing the corrosion of a metal is by supplying it with electrons, that is, by making it cathodic. This is done either by the use of impressed electrical currents or by sacrificial anodes.

1. Impressed Currents (a nonspontaneous reaction)

The use of impressed currents involves using an external source to supply electrons to the cathode while removing them from the anode. Ion migration through the ground water completes the circuit. An impressed direct current from a D.C. generator or an A.C. power source with a rectifier may be used. One terminal is connected to a relatively insoluble anode and the other to the metal work to be protected. The anode often consists of a mass of granular carbon pressed together between carbon bars. Since oxides of carbon are formed to some extent at the anode, the carbon rods need to be replaced occasionally. Other anodes that are sometimes used include scrap iron, lead alloys, and titanium coated with platinum.

Theoretically, it would be possible to use cathodic protection as the sole means of avoiding corrosion and thus dispense with protective coatings. To do this a very large current would be needed and the procedure would be very expensive. It is more economical to apply a reasonably good protective coating and then employ a relatively small current to prevent corrosion at the points where the surface coating is damaged.

One problem with using an impressed current provided by an external source is that some of the current may join another pipe which does not form part of the protection scheme. The unprotected pipe will act as the anode and will be badly corroded.



Cathodic Protection
Using Impressed Currents
Figure T9

METALLURGY AND CORROSION CATHODIC PROTECTION

eview of Five Step Method

In the ALCHEM unit on electrochemistry, a method was presented for predicting the most likely redox reaction in a given system. This method can be used to predict corrosion reactions when two different metals are in contact with the same electrolyte.

Example:

Predict the reactions which will occur when an iron pipe and a magnesium bar are joined with a wire. The iron pipe and the magnesium bar are in contact with ground water which contains dissolved oxygen.

Step 1:

List all the chemical species present. Use the *Relative Strengths of Oxidizing and Reducing Agents* table on the ALCHEM data sheet to identify all possible oxidizing agents (O.A.) and all possible reducing agents (R.A.).

Step 2:

Use the table to identify the strongest reducing agent (S.R.A.) and write its half reaction.

S.O.A. is
$$O_2(g) + H_2O(I)$$
.
 $O_2(g) + 2H_2O(I) + 4e^- \longrightarrow 4OH(aq)$
Gain of electrons is reduction at the cathode (GERC).

Step 3:

Use the reduction potential table to identify the strongest reducing agent (S.R.A.) and write its half reaction.

S.R.A. is
$$Mg(s)$$
.

 $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$

Loss of electrons is oxidation at the anode (LEOA).

Step 4:

Write the balanced net ionic equation.

cathode (GERC):
$$O_{2(g)} + 2H_2O_{(I)} + 4e^- \longrightarrow 4OH_{(aq)}$$

anode (LEOA): $2(Mg_{(s)} \longrightarrow Mg^{2^+}_{(aq)} + 2e^-)$
net reaction: $O_{2(g)} + 2H_2O_{(I)} + 2Mg_{(s)} \longrightarrow 4OH_{(aq)}^- + 2Mg^{2^+}_{(aq)}$

Step 5:

Determine whether or not the reaction is spontaneous.

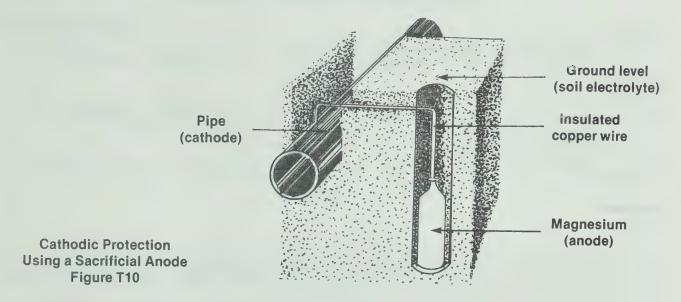
Since the oxidizing agent $(O_{2(g)}$ and $H_2O_{(f)}$) is listed *higher* in the oxidizing and reducing agents table than is the reducing agent $(Mg_{(S)})$, the reaction is *spontaneous*.

2. Sacrificial Anode (a spontaneous reaction)

The magnesium bar serves as the anode of the above cell since it is the site of oxidation. The electrons released by the oxidation of the magnesium flow along the wire to the iron pipe where the reduction reaction takes place. The iron pipe serves as the cathode in this cell since it is the site where reduction of the $O_2(g)$ and $H_2O(I)$ takes place. The iron itself does not take part in the reaction.

The example above illustrates the operation of a sacrificial anode. A sacrificial anode is made of a metal which is more easily oxidized than the metal to be protected. For example, when magnesium is attached to iron and both metals are in contact with the same electrolyte the magnesium will oxidize preferentially, thereby protec*'. It is the iron. Sacrificial anodes can be used to protect ships, as well as buried pipes and tanks. Figure T10 shows how a magnesium block can be used to protect an iron pipe.

METALLURGY AND CORROSION CATHODIC PROTECTION



The magnesium anode is buried at least 3 m from the pipe in a bed of sand to expedite the diffusion of anodic products in the ground water. The magnesium anode is connected to the iron pipe by means of a copper wire. As determined in the previous example, the following reaction takes place.

anode:
$$2(Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-})$$
cathode: $O_2(g) + 2H_2O(I) + 4e^{-} \longrightarrow 4OH(aq)$
overall: $2Mg(s) + O_2(g) + 2H_2O(I) \longrightarrow 2Mg^{2+}(aq) + 4OH(aq)$

The magnesium anode must be replaced periodically so it must be located where it is accessible for replacement and inspection.

The use of sacrificial anodes is effective only when the anode and the metal to be protected are in the same electrolyte. Ions must be free to migrate from one electrode to the other in order to complete the circuit.

Exercise:

- 1. What would be some of the factors to consider when deciding on the voltage to use in cathodic protection using impressed currents?
- 2. Write the equations for the reactions that would occur when using zinc as a sacrificial anode in protecting a buried steel tank. (What metals can be used as sacrificial anodes?)

- 3. Why bother with protective coatings when cathodic protection is available?
- 4. If 50 g of magnesium oxidized on a sacrificial anode during a 300 d period, what average current did it provide?

METALLURGY AND CORROSION PREVENTION OF CORROSION — DEMO T2

Purpose:

To study the effectiveness of different methods of preventing the corrosion of iron.

Materials:

- 8 100 mL beaker
- 4 5 x 100 mm iron strip
- 1 5 x 100 mm galvanized iron strip
- 1 5 x 100 mm tin-plated iron strip
- 1 5 x 100 mm painted iron strip
- 1 carbon rod

- 500 mL of 0.01 mol/L NaCl(aq) solution
- 80 mL concentrated HNO_{3 (aq)} Caution.
- 3 connecting wires c/w alligator chips
- 1 dry cell (1.5 V)
 - acetone
 - magnesium ribbon

Procedure:

Day 1:

- Pour about 70 mL of 0.01 mol/L NaCl solution into each of seven 100 mL beakers. 1.
- Pour about 80 mL of concentrated HNO_{3 (aq)} into a 100 mL beaker. Place an iron strip into the HNO_{3 (aq)} for about 2 min then remove it and rinse it with tap water. Caution: Concentrated HNO3 is corrosive.
- 3. Wash all of the strips with acetone and allow them to dry.
- 4. Place one of the iron strips into each of the seven beakers containing 0.01 mol/L NaCl(aq) solution.
- 5. Place a magnesium ribbon into one of the beakers containing an untreated strip of iron. Connect the iron strip to the magnesium ribbon by means of a connecting wire. Clip the strips to the side of the beaker so that the strips do not make direct contact.
- 6. Place a carbon rod into one of the other beakers containing an untreated strip of iron. Use connecting wires to join the negative terminal of the dry cell to the iron strip and the positive terminal of the dry cell to the carbon rod. Clip the strip and rod to the side of the beaker so a short circuit does not occur.
- Allow the beakers to stand overnight.

Day 2:

Record all the observations.

Observations:

Beaker	Observations	Explanation		
untreated from				
fron treated with HNO _{3 (aq)}				
iron attached to Mg				
iron attached to dry cell and carbon rod				
galvanized iron				
tin-plated iron				
nori beniac				

Questions:

Account for any reactions in terms of the theory of corrosion prevention.

METALLURGY AND CORROSION OVERVIEW

Overview Exercise

1.	List the metals used by ancient man and explain why they were the first metals isolated.
2.	Why did the Bronze Age occur before the Iron Age?
3.	The ancient alchemists were fascinated by the red pigment, cinnabar (HgS), to which they attributed mystical properties. When the red powder is heated gently in air it forms droplets of a silvery liquid. Continued heating forms a red powder again. Heating at a higher temperature produces more silvery droplets of liquid. Given that mercury(II) oxide is a red powder which is unstable above 300 °C, write equations that explain the behavior of cinnabar on heating.
4.	Name five sulfide ores which occur in Canada in commercial quantities. How are these ores treated before the metal is extracted?
5.	Explain the operation of a flotation cell.
6.	Calculate the mass of sulfur dioxide that would be produced by roasting 1.00 t of sphalerite, ZnS.

METALLURGY AND CORROSION OVERVIEW

7.	Calculate the minimum mass of carbon needed to reduce 1.00 kg of zinc from sufficient zinc oxide. (Assume carbon dioxide is the oxidation product of carbon.)
8.	In one stage of the refining of nickel, an aqueous solution containing nickel(II) ions has hydrogen gas injected into it under high pressure. The hydrogen gas reduces the nickel(II) ions to nickel atoms. What mass of hydrogen is needed to reduce 2.00 t of nickel in this process?
9	What mass of iron is needed to reduce all the copper(II) ions from 5000 L of a 0.00400 mol/L CuSO ₄ (aq) solution?
1	O. How long must a 12 A current run to release 4.86 kg of magnesium from an electrolytic cell containing molten magnesium chloride?

11.	Explain how a metal is electrolytically purified.
12.	What are the three types of alloys that can result when molten metals are mixed?
13.	In what general ways are alloys different from pure metals?
Write	equations for the corrosion reactions in Questions 14 through 18.
14.	A gardener disinfects a pair of steel pruning shears with mercury(II) chloride.
15.	Lead metal develops a protective coating of basic lead carbonate, PbCO ₃ • Pb(OH) ₂ , when exposed to the
	atmosphere for long periods. Write equations for the formation of this coating.
16.	An iron pipe is exposed to the wind and the rain.

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METALLURGY AND CORROSIO OVERVIEW

17.	An iron pipe used in an oil well is corroded by hydrogen sulfide.
18.	Chlorine used in a swimming pool corrodes a copper pipe.
19.	Explain why gold and silver are used to plate cheap jewellery and ornaments.
20.	What problems arise when the silver plate wears off a silver plated spoon?
21.	Explain how a passive surface can be formed on iron.
22.	Explain how an impressed current can be used to prevent corrosion.
23.	Explain how a sacrificial anode can be used to prevent corrosion.
24.	Could corrosion be stopped in a car by bolting a block of zinc or magnesium to the frame of the car? Explain.

6. Two Place Logs

| No. Log |
|---------|---------|---------|---------|----------|
| 1.0 .00 | 3.0 .48 | 5.0 .70 | 7.0 .85 | 9.0 .95 |
| 1.1 .04 | 3.1 .49 | 5.1 .71 | 7.1 .85 | 9.1 .96 |
| 1.2 .08 | 3.2 .51 | 5.2 .72 | 7.2 .86 | 9.2 .96 |
| 1.3 ,11 | 3.3 .52 | 5.3 .72 | 7.3 .86 | 9.3 .97 |
| 1.4 .15 | 3.4 .53 | 5.4 .73 | 7.4 .87 | 9.4 .97 |
| 1.5 .18 | 3.5 .54 | 5.5 .74 | 7.5 .88 | 9.5 .98 |
| 1.6 .20 | 3.6 .56 | 5.6 .75 | 7.6 .88 | 9.6 .98 |
| 1.7 .23 | 3.7 .57 | 5.7 .76 | 7.7 .89 | 9.7 .99 |
| 1.8 .26 | 3.8 .58 | 5.8 .76 | 7.8 .89 | 9.8 .99 |
| 1.9 .28 | 3.9 .59 | 5.9 .77 | 7.9 .90 | 9.9 1.00 |
| 2.0 .30 | 4.0 .60 | 6.0 .78 | 8.0 .90 | 1.00 .00 |
| 2.1 .32 | 4.1 .61 | 6.1 .79 | 8.1 .91 | 1.01 .00 |
| 2.2 .34 | 4.2 .62 | 6.2 .79 | 8.2 .91 | 1.02 .01 |
| 2.3 .36 | 4.3 .63 | 6.3 .80 | 8.3 .92 | 1.03 .01 |
| 2.4 .38 | 4.4 .64 | 6.4 .81 | 8.4 .92 | 1.04 .02 |
| 2.5 .40 | 4.5 .65 | 6.5 .81 | 8.5 .93 | 1.05 .02 |
| 2.6 .41 | 4.6 .66 | 6.6 .82 | 8.6 .93 | 1.06 .03 |
| 2.7 .43 | 4.7 .67 | 6.7 .83 | 8.7 .94 | 1.07 .03 |
| 2.8 .45 | 4.8 .68 | 6.8 .83 | 8.8 .94 | 1.08 .03 |
| 2.9 .46 | 4.9 .69 | 6.9 .84 | 8.9 .95 | 1.09 .04 |
| | | | | |



7. Solubilities

t = 25°C	P	= 101 kPa
HCI(aq)	*38%	12.4 mol/L
H ₃ PO _{4(aq)}	85%	14.7 mol/L
HNO _{3(aq)}	69%	15.4 mol/L
CH ₃ COOH(aq)	99.5%	17.4 mol/L
H ₂ 5O _{4(aq)}	94%	17.6 mol/L
NH ₃ (aq)	28%	14.8 mol/L
NaOH(aq)	50%	19.1 mol/L
AgCl(aq)		4.1 x 10 ⁻⁶ mol/L
CaCO _{3(aq)}		6.9 x 10 ⁻⁵ mol/L
Ca(OH) _{2(aq)}		6.9 x 10 ⁻³ mol/L
C ₁₂ H ₂₂ O _{11(aq)}		3.8 mol/L
NaCl(aq)		5.3 mol/L

ALCHEM Chemistry



data sheet

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8. Acid-Base Indicators at 25°C

Indicator	pH Range	HIn(aq)	In(aq)
methyl orange	3.1-4.4	red	yellow
methyl red	4.2-6.3	red	yellow
litmus	6.5-7.5	red	blue
bromthymol blue	6.0-7.6	yellow	blue
phenolphthalein	8.0-9.6	colorless	red
alizarin yellow	10.1-12.0	colorless	violet

Name of Base Species

hydrogen sulfate ion

hydrogen oxalate ion

hydrogen sulfite ion

O(aq)

perchlorate ion iodide ion bromide ion chloride ion

9 Relative Strengths of Acids and Rases

	Name of Acid Species	Percent Reaction of 0.10 mol/L Solution	Reaction of 0.10 mol/L Aqueous Acid Species with H ₂ O
g Acids 1	perchloric acid	100	$HClO_{4(aq)} + H_2O_{(\ell)} \xrightarrow{6} H_3O_{(aq)}^+ + ClO_{4(aq)}^-$
	hydroiodic acid	100	$HI_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O_{(aq)}^+ + I_{(aq)}^-$
	hydrobromic acid	100	$HBr_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O_{(aq)}^+ + Br_{(aq)}^-$
	hydrochloric acid	100	$HCl_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^{\dagger}_{(aq)} + Cl_{(aq)}$
Strong	nitric acid	100	$HNO_{3(aq)} + H_{2}O(\ell) \longrightarrow H_{3}O^{+}(aq) + NO_{3}(aq)$
	sulfuric acid	100	$H_2SO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O_{(aq)}^+ + HSO_{4(aq)}^-$
3	hydronium ion	100	$H_3O^+_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + H_2O_{(\ell)}$
,	oxalic acid	53	$HOOCCOOH_{(aq)} + H_2O(\ell)$ $\rightarrow H_3O^+_{(aq)} + HOOCCOO$
	sulfurous acid $(SO_{2(aq)} + H_2O_{(\ell)})$	32	$H_2SO_{3(aq)} + H_2O_{(\ell)} \rightarrow H_3O^{\dagger}_{(aq)} + HSO_{3(aq)}$
	hydrogen sulfate ion	29	$HSO_{4(aq)}^{-} + H_{2}O_{(\ell)} \longrightarrow H_{3}O^{+}_{(aq)} + SO_{4(aq)}^{2}$
	methyl orange ⁷	-	$HMO(aq) + H_2O(\ell) \rightarrow H_3O^{\dagger}(aq) + Mo(aq)$
	phosphoric acid	24	$H_3PO_{4(aq)} + H_2O_{(\ell)} \rightarrow H_3O^{+}_{(aq)} + H_2PO_{4(aq)}^{-}$
	hydrofluoric acid	8.2	$HF_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^{+}_{(aq)} + F_{(aq)}$
ds A	nitrous acid	7.3	$HNO_{2(aq)} + H_{2}O_{(\ell)} \rightarrow H_{3}O^{+}_{(aq)} + NO_{2(aq)}^{-}$
Decreasing Strength of Acids	bromthymol blue ⁷	-	$HBb_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Bb_{(aq)}$
gth c	benzoic acid	2.6	$C_6H_5COOH_{(aq)} + H_2O_{(\ell)} + H_3O^{+}_{(aq)} + C_6H_5$
Stre	hydrogen oxalate ion	2.3	HOOCCOO(aq) + H ₂ O(L) H ₃ O ⁺ (aq) + OOCC
asing	ethanoic (acetic) acid	1.3	CH ₃ COOH _(aq) + H ₂ O _(ℓ) H ₃ O ⁺ _(aq) + CH ₃ C
Decre	carbonic acid $(CO_{2(aq)} + H_2O_{(\ell)})$	0.21	$H_2CO_3(aq) + H_2O(\ell) - H_3O^+(aq) + HCO_3$
ī	phenolphthalein ⁷	_	$HPh_{(aq)} + H_2O_{(\ell)} - H_3O_{(aq)}^+ + Ph_{(aq)}^-$
	hydrogen sulfide	9.8 x 10 ⁻²	H ₂ S _(aq) + H ₂ O _(ℓ) ← H ₃ O ⁺ _(aq) + HS _(aq)
5	dihydrogen phosphate ion	7.9 x 10 ⁻²	$H_2PO_4(aq) + H_2O_{(\ell)} - H_3O_{(aq)}^+ + HPO_4^2$
	hydrogen sulfite ion	4.4 x 10 ⁻²	$HSO_{3(aq)}^{-} + H_{2}O_{(\ell)} - H_{3}O_{(aq)}^{+} + SO_{3(a}^{2}$
	ammonium ion	7.5 x 10 ⁻³	$NH_{4(aq)}^{+} + H_{2}O_{(\ell)} - H_{3}O_{(aq)}^{+} + NH_{3(aq)}$
	hydrogen carbonate ion	2.4 x 10 ⁻³	$HCO_{3(aq)}^{-} + H_{2}O_{(\ell)} \leftarrow H_{3}O_{(aq)}^{+} + CO_{3(aq)}^{2}$
	hydrogen phosphate ion	4.7 x 10 ⁻⁴	$HPO_{4(aq)}^{27} + H_2O_{(\ell)} - H_3O_{(aq)}^{+} + PO_{4(aq)}^{37}$
	hydrogen sulfide ion	3.3 x 10 ⁻⁴	$HS_{(aq)}^{-} + H_2O(\ell) - H_3O^{+}_{(aq)} + S^{2}_{(aq)}$
	water (55.5 mol/L)	1.8 x 10 ⁻³	$H_2O_{(\ell)} + H_2O_{(\ell)} - H_3O_{(aq)}^+ + OH_{(a}^-$
	hydroxide ion	0	$OH_{(aq)}^{2} + H_{2}O_{(\ell)} - H_{3}O_{(aq)}^{+} + O_{(aq)}^{2}$

- Notes:

 1. All strong acids are completely reacted and therefore written as $H_3O^+_{(aq)}$ plus the anion of the acid.

 2. All negative ions above water on the right side of the equation have essentially no ability to attract protons.

 3. The hydronium ion is only listed so that H_2O may appear as a base on the right side of the equation.

 4. $O^+_{(aq)}$ does not exist and is written as $OH^-_{(aq)}$.

 5. Quantitative acid-base reactions are those involving the reaction of

- H₃O[†](aq) with any base below with any acid above the hydr A single arrow is used for equ direction. In this acid-base ta tion of the 0.10 mol/L aqueo Indicators are not used as 0.16 empirically placed on the tab be made.

10. Formulas

$$n_{e'} = \frac{q}{Q} = \frac{k}{9.65 \times 10^4}$$

$$E_{(kW\cdot h)} = \frac{IVt}{1000}$$

$$E = IV$$

11. SI Units & **Symbols**

metre.						m
gram .						g
tonne.						t
mole .						mol
litre						L
second						S
						A

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103 (257)

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ELEMENTS